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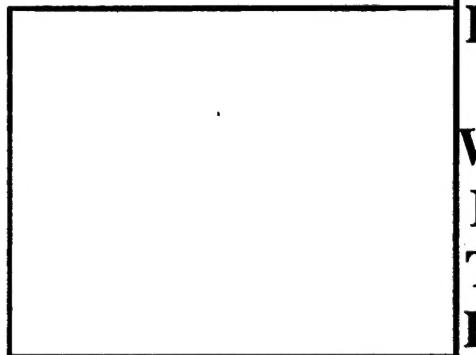
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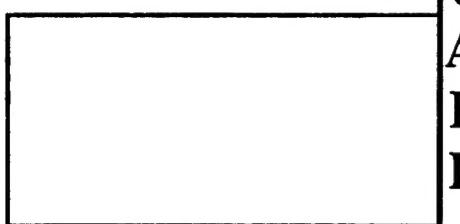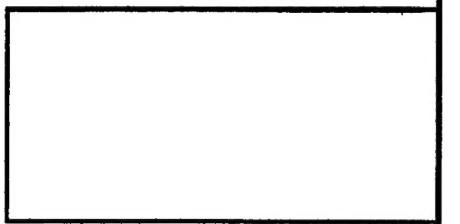
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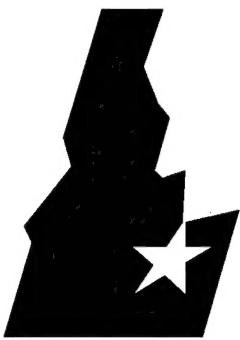
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Intrinsic Bioattenuation of JP-4 Jet Fuel Constituents in Groundwater at March Air Force Base Operable Unit 3

John F. Keck
Allan H. Wylie
Thomas A. Matzen

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Intrinsic Bioattenuation of JP-4 Jet Fuel Constituents in Groundwater at March Air Force Base Operable Unit 3

John F. Keck
Allan H. Wylie
Thomas A. Matzen

AQM01-01-0304

ABSTRACT

This report describes efforts to determine whether or not intrinsic bioattenuation occurs at significant rates and extents in the shallow aquifer at Operable Unit 3 at March Air Force Base (AFB), California. The aquifer is contaminated with benzene, toluene, ethylbenzene and xylenes (BTEX) resulting from releases of JP-4 jet fuel from an aircraft refueling system.

Efforts focused on use of existing quarterly groundwater monitoring data and data from a Comprehensive Environmental Response, Compensation and Liability Act Remedial Investigation performed from 1991 through 1994. A technical protocol published by the Air Force Center for Environmental Excellence to determine the rate and extent of intrinsic bioattenuation was followed where applicable data exist.

Three hypotheses were tested in a phased approach:

1. Intrinsic bioattenuation occurs in groundwater at March AFB Operable Unit (OU) 3

2. Intrinsic bioattenuation occurs in groundwater at OU 3 at rates and extents such that receptors will not be affected

3. Intrinsic bioattenuation occurs at rates and extents such that the aquifer will eventually be restored to background water quality.

The three hypotheses were tested by analyzing existing data including microbial studies; distributions of nutrients, contaminants, electron acceptors and byproducts; and statistically correlating concentrations of electron acceptors and biodegradation byproducts between contaminated and uncontaminated wells using an analysis of variance. Rates of contaminant bioattenuation were estimated by comparing contaminant concentrations in groundwater monitoring wells located approximately along groundwater flow lines.

Results of the analysis indicate that intrinsic bioattenuation of BTEX does occur in the OU 3 aquifer at rates and extents such that no migration outside the confines of the operable unit is likely to occur. Uncontaminated groundwater that enters the area from upgradient contains sufficient concentrations of electron acceptors to degrade essentially all of the BTEX that dissolves into groundwater from the free-phase fuel source. The analysis of variance provided evidence that dissolved oxygen, nitrate, and sulfate are all used in microbial metabolism of BTEX in the OU 3 aquifer. A first-order intrinsic bioattenuation rate for BTEX of 0.8992 year^{-1}, and a half-life of 0.77 years were estimated for one well pair. However, given that free-phase fuel covers a large area at OU 3, and assuming that no biodegradation occurs within the free-phase fuel, this report concludes that intrinsic bioattenuation alone will not restore the entire aquifer to beneficial use in the near future. Nor will any other remedial approach.

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FIGURES

TABLES

ACRONYMS

ACOE	Army Corp of Engineers
AFB	Air Force Base
AFCEE	U.S. Air Force Center for Environmental Excellence
ANOVA	analysis of variance
bgs	below ground surface
BTEX	benzene, toluene, ethylbenzene, and xylene
CFR	Code of Federal Regulations
DO	dissolved oxygen
EPA	U.S. Environmental Protection Agency
INEL	Idaho National Engineering Laboratory
MCL	maximum contaminant level
OU	operable unit
PRG	preliminary remediation goal
TDS	total dissolved solids
TKN	Total Kjeldahl Nitrogen
TPH	total petroleum hydrocarbons
USCS	Unified Soil Classification System

INTRINSIC BIOATTENUATION OF JP-4 JET FUEL CONSTITUENTS IN GROUNDWATER AT MARCH AIR FORCE BASE OPERABLE UNIT 3

1. INTRODUCTION

This report describes efforts to determine whether or not intrinsic bioattenuation occurs at significant rates and extents in the shallow aquifer at Operable Unit (OU) 3 at March Air Force Base (AFB), California. The aquifer is contaminated with benzene, toluene, ethylbenzene, and xylenes (BTEX) resulting from releases of JP-4 jet fuel from an aircraft refueling system. Petroleum hydrocarbons including jet fuel are ubiquitous environmental contaminants. Fuels like JP-4 are complex solutions of hundreds of individual compounds that vary in their volatility, aqueous solubility, density, and other properties. When these compounds are released into the environment as a result of fuel spills, they are subject to processes including volatilization, solubilization, advection, dispersion, diffusion, adsorption, abiotic degradation, and biodegradation. Nearly all fuel constituents can be utilized as food sources by bacteria present in the environment. Biodegradation of fuel hydrocarbons has found increasing acceptance as a means of remediating fuel-contaminated soil and groundwater.

The primary contaminants of concern in JP-4 jet fuel are BTEX. These compounds dissolve in water at slight but significant concentrations. Benzene, a known human carcinogen, presents the highest human health risk. Other fuel constituents include polycyclic aromatic hydrocarbons including naphthalene; aliphatics including pentane, hexane, heptane, octane, nonane; and other compounds.

Hydrocarbon-degrading microbes break down hydrocarbon molecules, releasing electrons in the process. Electrons are cycled through energy-producing metabolic pathways. A terminal electron acceptor is required at the end of the process. Aerobic microbes use oxygen as a terminal electron acceptor. Anaerobic microbes may use nitrate, sulfate, carbon dioxide, iron, or other compounds. The stoichiometry for benzene biodegradation using various electron acceptors is shown in Table 1. Nutrients are also required to supply material for cell-building, primarily nitrogen and phosphorus.

Petroleum hydrocarbons including JP-4 constituents are biodegraded in the environment by naturally-occurring microorganisms. Land application or land farming of petroleum wastes has been used for years as a method of disposing of these wastes. This process involves spreading both liquid and solid wastes on soil surfaces and adding nutrients and tilling as needed to stimulate biodegradation. Oil refinery wastes applied to soils at over 10% of the soil weight per year can be completely degraded in less than 1 year.

Raymond (1976) found that BTEX compounds in groundwater were aerobically biodegradable and developed an in situ process for remediating petroleum hydrocarbon-contaminated groundwater. Raymond used recirculation of nutrient-amended water to maintain high nutrient and electron acceptor concentrations.

Many subsequent studies have determined rates and extents of BTEX biodegradation under both laboratory and in situ conditions for many different nutrient, substrate, and electron acceptor conditions. Typically, it has been found that a mixed microbial population of several species is required to completely metabolize aromatic hydrocarbons to carbon dioxide and water. These types of mixed microbial populations typically exist in soil and groundwater. Past studies indicated that benzene was only biodegraded aerobically; however, more recent studies indicate that benzene may be biodegraded under sulfate-reducing conditions.

Table 1. Simplified stoichiometry, electron acceptor-to-contaminant ratios and types of reactions for BTEX biodegradation reactions (after Wiedemeir et al. 1995). Stoichiometry does not account for cell production.

Benzene biodegradation reaction	Mass ratio of electron acceptor to benzene	Average mass ratio of electron acceptor to total BTEX	Type of reaction
$7.5O_2 + C_6H_6 \rightarrow 6CO_{2,g} + 3H_2O$	3.1:1	3.14:1	Benzene oxidation/aerobic respiration
$6NO_3^- + 6H^+ + C_6H_6 \rightarrow 6CO_{2,g} + 6H_2O + 3N_{2,g}$	4.8:1	4.9:1	Benzene oxidation/ denitrification
$6OH^+ + 30Fe(OH)_3 + C_6H_6 \rightarrow 6CO_2 + 30Fe^{+2} + 78H_2O$	41.1:1		Benzene oxidation/iron reduction
$7.5H^+ + 3.75SO_4^{-2} + C_6H_6 \rightarrow 6CO_{2,g} + 3.75H_2S + 3H_2O$	4.6:1	4.7:1	Benzene oxidation/sulfate reduction
$4.5H_2O + C_6H_6 \rightarrow 2.25CO_{2,g} + 3.75CH_4$	NA		Benzene oxidation/ methanogenesis

Byproducts of aerobic respiration of petroleum hydrocarbons may include dissolved carbon dioxide present as bicarbonate (HCO_3^-) and carbonate (CO_3^{-2}). Byproducts of anaerobic respiration may include increased pH, methane, and hydrogen sulfide.

The natural history of a fuel release, such as occurred at OU 3 over a period of years, may be described as follows:

1. Fuel is released from tanks and piping at or belowground surface. Fuel infiltrates into soil, eventually reaching the water table.

2. Fuel, less dense than water, ponds on the water table, eventually depressing it and forming a "pancake" of fuel.

3. Soluble fuel constituents slowly dissolve out of the fuel into groundwater. Seasonal water table fluctuations result in formation of a smeared zone below the water table, resulting in a larger fuel-to-water contact area and increased rate and extent of contaminant solubilization.

4. A contaminant plume of solubilized fuel constituents in groundwater forms and migrates downgradient with advected groundwater. Dissolved fuel constituents are subject to processes including volatilization, advection, dilution, dispersion, adsorption, and biodegradation.

5. Naturally-occurring aerobic microorganisms biodegrade contaminants in the plume. Oxygen in groundwater, with a maximum solubility of about 8 mg/L, is utilized faster than it can be replaced. Soon the groundwater in the areas of highest contaminant concentrations becomes anaerobic, with oxygen concentrations less than 1 mg/L.

6. Anaerobic bacteria, using nitrate and sulfate dissolved in groundwater as a terminal electron acceptor, continue to biodegrade contaminants. As nitrate and sulfate are expended, carbon dioxide may be utilized.

7. Aerobic biodegradation continues at the periphery of the plume, where contaminant concentrations are lower and oxygen concentrations are higher.

8. Meanwhile, dispersion and diffusion act to dilute contaminant concentrations. Eventually the plume stops expanding and stabilizes. Replacement of contaminants from the source is balanced by intrinsic bioattenuation processes including biodegradation, adsorpton, diffusion, and dispersion until a steady-state condition of no further plume migration is established.

9. If the source is contained and removed, by free product recovery or other means, the plume eventually begins to contract as the net effect of intrinsic bioattenuation processes exceeds dissolution rates.

While intrinsic bioattenuation has long been known to occur, only recently has it been seriously considered as a remedial alternative for hydrocarbon-contaminated groundwater. Several realizations on the parts of scientists, engineers, and administrators have brought this about, including

1. The realization that much of the contaminated groundwater cannot be cleaned up at present. Experts in the field of hydrogeology (Bredehoeft 1992, Keely 1989) agree that occurrence of nonaqueous phase liquids, low-permeability and/or heterogeneous aquifer media, and other site conditions may make cleaning up contaminated groundwater at many sites impossible, regardless of cost.

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2. Computer models are now available that allow for estimating the time required for intrinsic bioattenuation to achieve stabilization and cleanup of contaminant plumes.

3. The U.S. Air Force Center for Environmental Excellence (AFCEE), in collaboration with the U.S. Environmental Protection Agency (EPA), R. S. Kerr Environmental Research Laboratory, and other agencies, has developed a protocol for assessing the site-specific effectiveness of intrinsic bioattenuation for remediation. This initiative has stimulated interest and research in this natural phenomenon in the United States and Canada.

4. The U.S. National Research Council (1993) published guidelines for documenting intrinsic or engineered biodegradation processes. These guidelines suggest that researchers demonstrate that

   a. Concentrations of constituents of concern are decreasing over time

   b. Microorganisms capable of degrading the constituents of concern are present at the site

   c. Biodegradation is occurring.

2. OBJECTIVES

The objectives of this study are to use the U.S. Nuclear Regulatory Commission and AFCEE guidelines to determine whether or not intrinsic bioattenuation is occurring at March AFB OU 3. Specific objectives are defined in three phases: (1) to test the hypothesis that intrinsic bioattenuation occurs in groundwater at March AFB OU 3, (2) if (1) is accepted, then to test the hypothesis that intrinsic bioattenuation occurs in groundwater at March AFB OU 3 at rates and extents such that receptors will not be affected, and (3) if (2) is accepted, to test the hypothesis that intrinsic bioattenuation occurs at rates and extents such that the aquifer will eventually be restored to background water quality. Analysis of existing groundwater monitoring data and groundwater fate and transport modeling will be used to make the determinations.

3. BACKGROUND

3.1 Location

March AFB is located on 7,123 acres at the north end of Perris Valley in Riverside County, California. The base is approximately 60 miles east of Los Angeles and 90 miles north of San Diego in Perris Valley (Figure 1). Perris Valley is a semiarid, north-south trending alluvial valley bounded by low-lying granitic bedrock on the west, and a series of tributary valleys and granitic mountains on the east.

The Panero aircraft refueling system site occupies approximately 45 acres on the eastern half of March AFB (Figure 2). This area of the base is entirely covered with either concrete or relatively small areas of asphalt. Surface features at the site consist of two 1.5-million-gal aboveground fuel tanks with a surrounding secondary containment berm and the associated newly constructed pump house. The aboveground tanks, secondary containment berm, and pumphouse were constructed in 1992–1993.

3.2 Site History

March AFB began its existence on March 1, 1918, as a 640-acre facility known as the Alessandro Aviation Field. With the exception of the period 1923 to 1927, March AFB has been in continuous operation since 1918.

In 1949, the Strategic Air Command took control of March AFB. By mid-1950, March AFB was being used primarily as a bomber base for B-47 bombers of the 22nd Bombardment Wing. In the mid-1960s, the 909th Air Refueling Squadron and 486th Bombardment Squadron were transferred to March AFB. During the late 1960s, the 303rd Air Rescue Squadron and 452nd Military Airlift Wing were also transferred to March AFB.

In the early 1970s, the 486th and 909th tactical squadrons were removed from duty at March AFB. During the mid-1970s, the 452nd Air Refueling Wing converted from C-119s to C124s, then to C-130s, and finally to KC-135s.

On October 1982, the 22nd Bombardment Wing was redesignated the 22nd Air Refueling Wing. The refueling wing was notified that B-52 bombers would be retired from service and that the wing would receive KC-10A Extender tankers to supplement the existing KC135s assigned to the base. In June 1992, Headquarters-Air Mobility Command based at Scott AFB, Illinois, took over command of March AFB. The 22nd Air Refueling Wing is the primary mission of March AFB.

The Panero aircraft refueling system included an underground tank farm comprised of 34 50,000-gal steel underground storage tanks, one 25,000-gal steel underground defueling tank, a 550-gal steel underground vapor recovery tank, a pump house consisting of 34 600-gpm jet fuel pumps, and approximately 7,500 ft of associated underground steel piping used to deliver fuel to and from fueling hydrants (Figure 3). The Panero system received fuel from the bulk fuel storage area located approximately 6,000 ft northwest of the Panero site via steel underground fuel transfer piping. A total of 10 dual hydrant lateral control pits and 20 refueling hydrants were located along the length of the Panero site. Fuel was pumped to the refueling hydrants from the pump house located at ground surface immediately above the underground tank farm. Excess fuel remaining in the fuel distribution lines following refueling activities drained to one of two locations. Southeast of the pump house, the fuel drained via the defueling line to the 25,000-gal defueling tank located at the southeast end of the site.
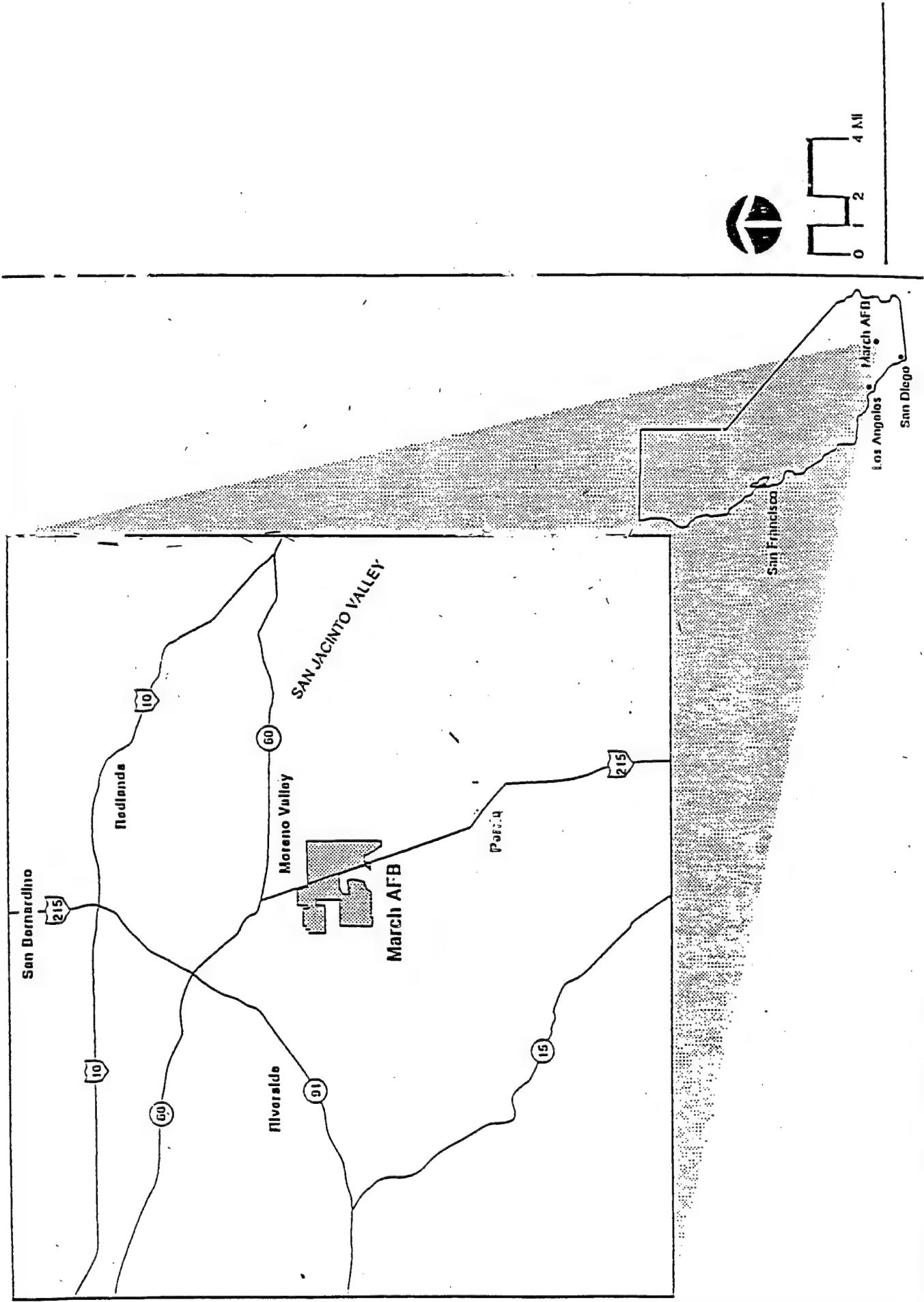
**Figure 1.** Location of March AFB.

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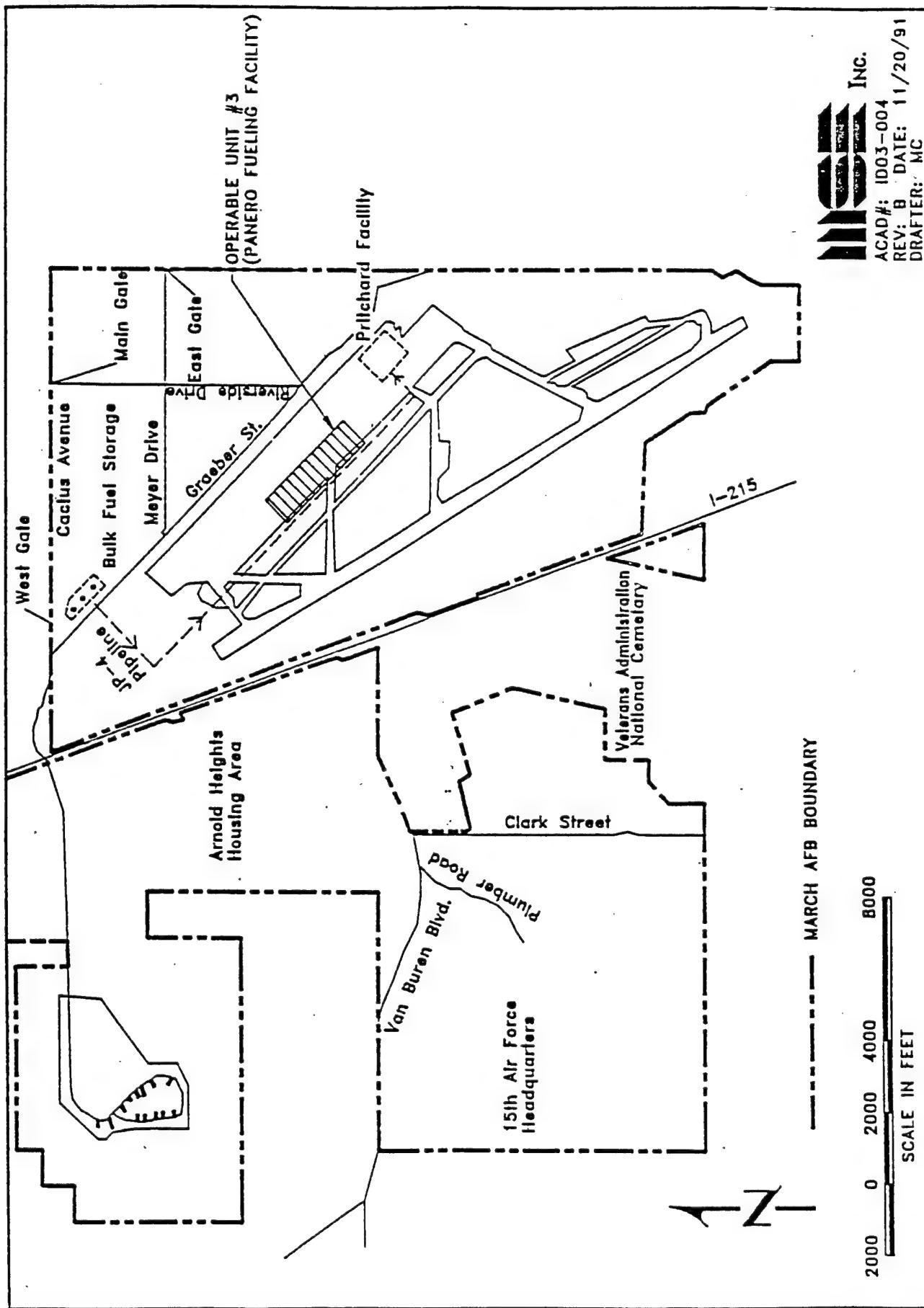
**Figure 2.** Location of the Panero site (OU 3) at March AFB.
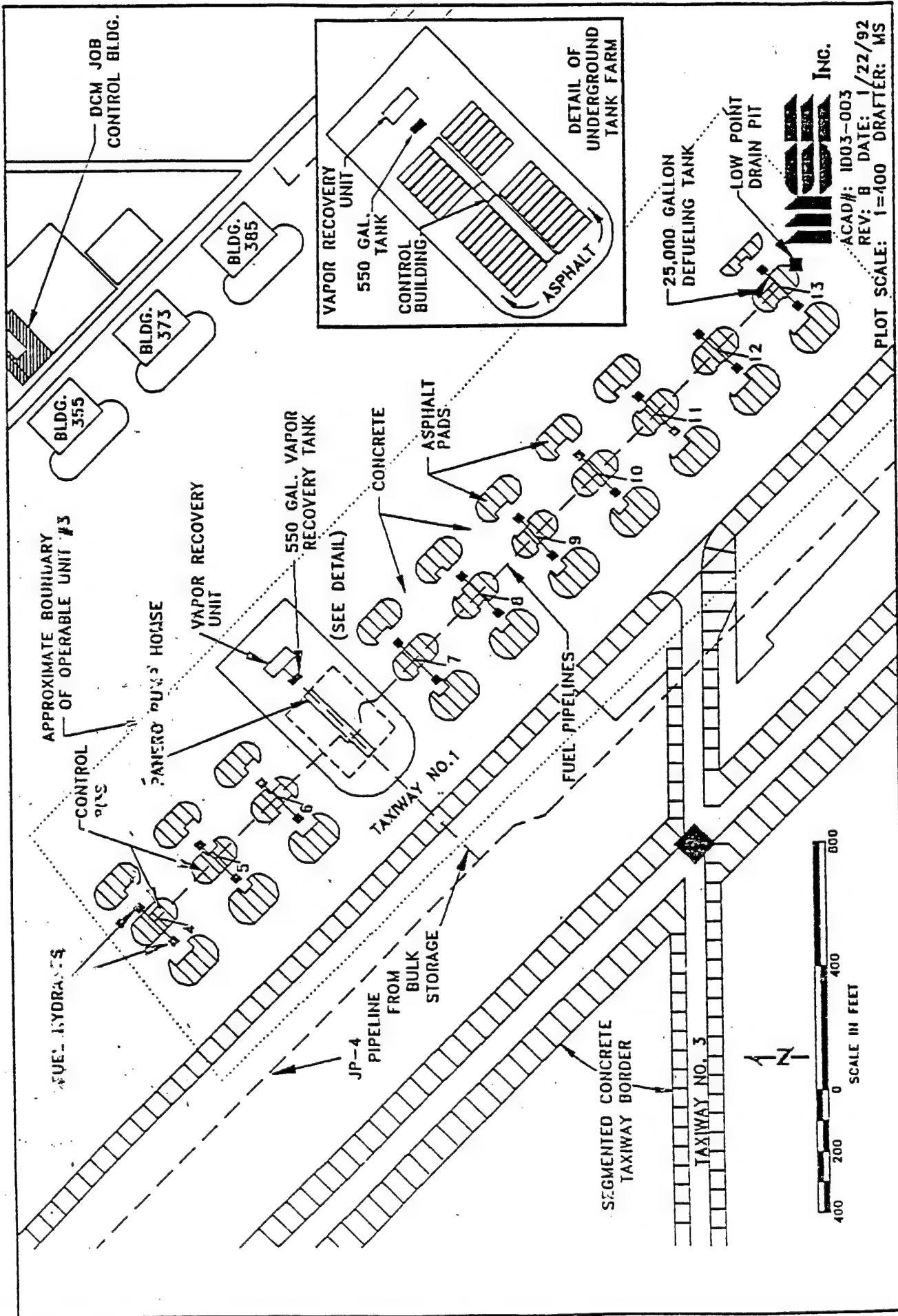
Figure 3. Panero aircraft refueling system site.

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The fuel that accumulated in the 25,000-gal defueling tank was then pumped back to the pump house (into Tank 20) via the return line. Therefore, three separate pipelines were present at the facility to the southeast of the pump house. The three pipelines were vertically aligned and spaced approximately 1 ft apart in a filled trench beneath the control pits. The fuel lines, with the exception of the defueling line, ran from the pump house to control pit 13 at the southeast end of the facility. The defueling line ran between control pits 7 and 13. Excess fuel in the fuel distribution lines to the northwest of the pump house drained back by gravity to the pump house (Tank 19) via a return line. Thus, only two pipelines were present at the facility to the northwest of the pump house. These two lines were also vertically aligned in a filled trench beneath the control pits and ran between the pump house and control pit 4 and the northwest end of the facility.

3.3 Geology

Soils beneath the site consist of alluvial deposits eroded from the surrounding higher bedrock terrain. Soils are quite heterogeneous and are probably representative of coalesced alluvial fans deposited in the Perris and Moreno valleys. The alluvial deposits consist of alternating discontinuous layers of fine-to-coarse grained unconsolidated to occasionally semiconsolidated material. Cross sections of OU 3 lithologies as determined by examination of drill cuttings are shown in Appendix A, Figures A-28 and A-29.

Soil grain sizes range from very fine gravels (0.08 to 0.16 in. diameter) to silts and clays (≤ 0.002 in. diameter). Unified Soil Classification System (USCS) classifications range from GP (poorly graded gravels, gravel-sand mixtures, or sand-gravel-cobble mixtures) to ML (inorganic silts, clayey silts with slight plasticity). The predominant USCS soil type at the Panero Site is SM (silty sands, sand-silt mixtures). Generally, the soils seem to coarsen with depth. Sands and fine gravels with less silt become more common below 50 to 60 ft.

Grain density values ranged from 2.64 to 2.73 g/cm^3. Average grain density is 2.69 g/cm^3. Bulk density values ranged from 1.62 to 2.14 g/cm^3. Average bulk density is 1.93 g/cm^3.

Air permeability values determined in situ at Panero range from 25 darcies as measured in EX-01 to 29 darcies as measured in TF-09. Horizontal radius of influence, as determined by the presence of a measurable differential pressure, was over 210 ft.

Granodiorite bedrock was encountered at a depth of 194-ft below ground surface (bgs) in well PANPW-1 at the southeast end of the site. A thin weathered rock zone exists at the bedrock-alluvium contact. It is assumed that the buried bedrock surface is topographically similar to the granodiorite outcrops on the west side of March AFB. No obvious jointing system is visible in the bedrock outcrops on the west side of March AFB; however, it is possible that weathering has obscured the jointing. Joint systems are visible in the bedrock north of the base on the north side of the valley. It may be assumed that these joint systems are continuous throughout the Moreno Valley area. The bedrock has an irregular surface probably consisting of a series of sediment-filled stream channels with a general slope towards the east and the middle of the Perris Valley.

3.4 Hydrogeology

Average depth to groundwater at the Panero site is about 40 ft. Groundwater contour mapping for March AFB indicates that the water table in the immediate area of OU 3 is relatively flat. Water levels from wells containing free product were not used. Groundwater currently flows generally from northwest to southeast at OU 3. The water table gradient varies from 0.0058 to 0.0033 ft/ft with a median of 0.0046 ft/ft. An upward gradient of -0.00118 was calculated for a well pair at OU 3.

Numerous slug tests and pumping tests were conducted at OU 3 to determine aquifer hydraulic conductivity in the upper part of the aquifer. Analyses of these tests indicate that hydraulic conductivity at the Panero site is probably log-normally distributed. The geometric mean hydraulic conductivity is 2.7 ft/day, and the mode is 4.9 ft/day. Using the median gradient of 0.0046, the geometric mean hydraulic conductivity of 2.7 ft/day and assuming an effective porosity of 0.25, the calculated groundwater velocity is 21 ft/yr. Using the median gradient of 0.0046 and the most common (mode) hydraulic conductivity of 4.9 ft/day and assuming an effective porosity of 0.25, the calculated groundwater velocity is 33 ft/yr.

3.5 Nature and Extent of Contamination

A detailed description of the nature and extent of contamination at OU 3 is provided in the remedial investigation report (INEL 1994) and is summarized here. Operable Unit 3 includes the former Panero Fueling Area and is one of three OUs at March AFB. Contaminants of concern at OU 3 include JP-4 jet fuel constituents BTEX and chloroform, trichloroethene, tetrachloroethene, and manganese.

3.6 Unsaturated Zone Contamination

The primary source of contamination at OU 3 is release of JP-4 jet fuel from underground storage tanks and associated piping. The tanks have been removed, and the piping has been removed or grouted in place. Soils in the former tank farm area were excavated to a depth of 20 ft bgs, thermally treated to volatilize and destroy organic contaminants, and returned to the excavation. No fuel releases are known to have occurred after the tank removal.

Table 2 shows descriptive statistics for metals and organics in soil. Contaminants detected in shallow soils (between the ground surface and 20 ft bgs) include BTEX, acetone, and methylene chloride. Contour maps illustrating the extent of soil contamination by total petroleum hydrocarbons (TPH), BTEX, acetone, and methylene chloride are contained in Appendix A. Cross sections showing vertical profiles of soil contamination are also provided in Appendix A.

3.7 Groundwater Contamination

Free product recovery was initiated as a Comprehensive Environmental Response, Compensation, and Liability Act Non-Time Critical Removal Action and will be continued as part of an overall remedial action. Initially, mobile skimming pumps were operated from July 1990 to July 1993 in wells PANMW-01, MW-03, and MW-04. Total fuel recovered by skimming was approximately 7,300 gal. Dual-phase fuel recovery was initiated in June 1994, using wells PANEX-02 and EX-04. Fuel recovery by dual-phase pumping from June 1994 to March 1995 was approximately 1,825 gal. Mobile skimmers are being deployed to increase yields. Also, AFCEE will test bioslurper wells at OU 3 in 1996 to determine fuel recovery rates using vacuum dewatering wells.

The occurrence of free product on the water table is complicated by a steady rise in water table levels since approximately 1984, when March AFB production wells were shut down. Monitoring of base-wide groundwater levels indicates that groundwater elevations have risen by an average of 7.40 ft since 1987. Assuming the groundwater began rising in 1984 and that the rate of groundwater rise has been constant through December 1992, the groundwater has potentially risen approximately 11.5 ft. Groundwater

Table 2. Descriptive statistics for metals and organics detected in soil at OU 3.

Compound	Number of samples	Arithmetic mean (µg/kg)	Standard deviation (µg/kg)	Minimum[a] (µg/kg)	Maximum[a] (µg/kg)
1,1-dichloroethene	406	2,502	7,009	0	68000.000
2-butanone[b]	406	2,513	7,011	0	68000.000
2-hexanone	406	2,680	7,561	0	68000.000
2-methylnaphthalene	175	1,826	13,753	0	180000.000
4-methyl-2-pentanone	406	2,502	7,009	0	68000.000
Acenaphthene	300	760	3,540	0	57090.000
Acetone[b]	406	2,792	7,522	0	68000.000
Aluminum	11	8,694	5,593	0	17500.000
Anthracene	300	478	3,358	0	57090.000
Antimony	11	4	2	0	10.000
Arsenic	11	1	0	0	2.000
Ethylmethylbenzene	60	18,291	19,690	0	110000.000
Methylethylbenzene	1	53	0	0	53.000
Methylpropylbenzene	2	41	18	0	54.000
Ethyldimethylbenzene	1	110	0	0	110.000
Trimethylbenzene	2	4,292	5,952	0	8500.000
Barium	11	112	63	0	202.000
Benzene	406	4,353	14,482	0	170000.000
Benzo(a)anthracene	300	497	3,357	0	57090.000
Benzo(a)pyrene	272	546	3,524	0	57090.000
Benzo(b)fluoranthene	300	486	3,358	0	57090.000
Benzo(g,h,i)perylene	300	523	3,360	0	57090.000
Benzo(k)fluoranthene	300	477	3,358	0	57090.000
Benzoic acid	169	3,940	21,570	0	276800.000
Beryllium	11	0	0	0	1.000
Tetramethylcyclohexane	1	48	0	0	48.000
Cadmium	11	0	0	0	1.000
Calcium	11	1,625	953	0	3380.000
Chlorobenzene	406	2,503	7,009	0	68000.000
Chloroform[b]	406	2,113	6,670	0	68000.000
Chromium	11	5	4	0	13.000

Table 2. (continued).

Compound	Number of samples	Arithmetic mean (µg/kg)	Standard deviation (µg/kg)	Minimum[a] (µg/kg)	Maximum[a] (µg/kg)
Chrysene	300	513	3,358	0	57090.000
Cobalt	11	6	3	0	12.000
Copper	11	14	5	0	20.000
Cyanide	11	1	0	0	1.000
Di-n-butylphthalate	173	809	4,397	0	57090.000
Di-n-octylphthalate	173	810	4,397	0	57090.000
Dibenz(a,h)anthracene	300	520	3,359	0	57090.000
Dibenzofuran	173	801	4,398	0	57090.000
Ethylbenzene	406	10,221	24,750	0	220000.000
Fluoranthene	300	503	3,362	0	57090.000
Fluorene	300	311	774	0	11600.000
Hexane	7	5,560	10,959	0	29000.000
Indeno(1,2,3-cd)pyrene	300	484	3,357	0	57090.000
Iron	11	14,815	9,358	0	30200.000
Lead	11	3	1	0	5.000
Magnesium	11	3,189	2,153	0	6080.000
Manganese	11	328	188	0	706.000
Mercury	8	0	0	0	0.000
Methylene chloride[b]	406	2,425	6,970	0	68000.000
Dimethylnaphathalene	1	7	0	0	7.000
Naphthalene	302	1,097	6,625	0	110000.000
Nickel	11	4	1	0	6.000
Phenanthrene	300	554	3,368	0	57090.000
Phenol	175	817	4,372	0	57090.000
Potassium	11	3,943	2,669	0	8410.000
Pyrene	300	551	3,365	0	57090.000
Selenium	11	0	0	0	0.000
Silver	11	0	0	0	1.000
Sodium	11	319	100	0	481.000
Tetrachlorethene	406	2,501	7,009	0	68000.000
Thallium	11	0	0	0	1.000

Table 2. (continued).

Compound	Number of samples	Arithmetic mean (µg/kg)	Standard deviation (µg/kg)	Minimum[a] (µg/kg)	Maximum[a] (µg/kg)
Toluene	406	28,216	85,057	0	960000.000
Trichloroethene	406	2,501	7,009	0	68000.000
Vanadium	11	27	18	0	53.000
Xylene (total)	406	55,140	129,479	0	1100000.000
Zinc	11	38	21	0	79.000
bis(2-ethylhexyl)phthalate[b]	173	681	4,331	0	57090.000

a. Soil concentrations are from Black and Veatch (1993).

b.

Compound	Fraction of total samples with "BJ" qualification flags (%)
2-butanone	16.99
Acetone	11.82
Chloroform	16.99
Methylene chloride	2.96
bis(2-ethylhexyl)phthalate	1.73

fluctuations result in fuel being trapped below the water table as residual saturation. Residual saturation is liquid phase hydrocarbon held in pores by capillary forces. Residual saturation is not recoverable by pumping. It is assumed that most of the hydrocarbons dissolved in the groundwater, called the dissolved-phase plume, are derived from pockets of residual JP-4 that lie below the water table because residual fuel below the water table has a much larger total surface area than the free product floating on the surface of the water table. Total petroleum hydrocarbon values in excess of 10,000 ppm in soil are considered to be indicative of residual fuel saturation.

Risk-based contaminants of concern with maximum concentrations detected in groundwater at OU 3 and California maximum contaminant levels (MCLs) are listed in Table 3. Summary statistical analyses of the contaminants detected in groundwater are presented in Tables 4a and 4b. Figure 4 illustrates the areal extent of benzene contamination in groundwater at OU 3 in September 1992. Isopleths of benzene contamination are presented because benzene is the most soluble of the compounds detected and because benzene accounts for 95.53% of the carcinogenic risk at OU 3. The dissolved-phase BTEX contaminant plume at OU 3 has not migrated significant distances downgradient from the free-product source. Contaminant isopleth maps for BTEX detected in groundwater at OU 3 for sampling quarters 2 through 9 (9/92 through 10/94) are presented in Appendix A.

Figure A-16 shows monitoring well locations at the Panero area. Thirteen wells have measurable free product in them. These are EX-02, FP-05, MW-05, MW-01, MW-03, MW-15, TF-01, TF-02, TF-06, TF-09, TF-11, and TF-12. A series of isopleth maps showing apparent free product thickness from March

Table 3. Contaminants detected in groundwater at the Panero site, maximum unqualified concentrations, and EPA and California MCLs (Black and Veatch 1993).

Chemicals	Maximum unqualified concentration (µg/L)	EPA MCLs[a] (µg/L)	California MCLs[b] (µg/L)
Toxic			
Acetone	5.6E+03	Not listed	Not listed
Bromoform	1.0E+01	1.0E+02[c]	1.0E+02[c]
Bromodichloromethane	1.5E+01	1.0E+02[c]	1.0E+02[c]
Chloroform	1.1E+01	1.0E+02[c]	1.0E+02[c]
Dibromochloromethane	2.6E+01	1.0E+02[c]	1.0E+02[c]
Ethylbenzene	1.5E+03	7.0E+02	6.8E+02
Methylene chloride	1.8E+03	5.0	4.0E+01
Manganese	2.17E+04	Not listed	Not listed
Tetrachloroethene	4.5E+01	5.0	5.0
Toluene	1.5E+04	1.0E+03	Not listed
Trichloroethene	7.7E+01	5.0	5.0
Xylene	7.6E+03	1.0E+04	1.75E+03
Carcinogenic			
Benzene	1.4E+04	5.0	1.0
Bromoform	1.0E+01	1.0E+02[c]	1.0E+02
Bromodichloromethane	1.5E+01	1.0E+02[c]	1.0E+02[c]
Chloroform	1.1E+01	1.0E+02[c]	1.0E+02[c]

a. 40 Code of Federal Regulations (CFR) 141.12 and 141.61, "Maximum Contaminant Levels for Organic Chemicals."

b. California CFR, Title 22, Division 4, Chapter 15, Article 4, Section 64435, "Maximum Contaminant Levels for Organic Contaminants."

c. Total trihalomethanes = Σ bromodichloromethane, dibromochloromethane, bromoform, and chloroform.

Table 4a. Descriptive statistics for chemicals detected in groundwater at the Panero site.

Compound	Number of samples	Arithmetic mean (μg/L)	Standard deviation (μg/L)	Minimum[a] (μg/L)	Maximum[a] (μg/L)
1,1,1-trichloroethane	72	207	363	2	1,000
1,1-dichloroethane	72	206	364	0	1,000
1-dihydromethylindene	1	70	0	0	70
2-butanone	72	207	363	0	1,000
Acetone[b]	72	316	792	0	5,600
Ethylmethylbenzene	29	364	342	0	1,000
Trimethylbenzene	3	141	137	0	300
Benzene, trimethyl isomer	5	494	517	0	1,300
Benzene	72	2,290	4,218	0	14,000
Bromodichloromethane	72	207	363	0	1,000
Bromoform	72	207	363	0	1,000
Cyclopentane	1	66	0	0	66
Cyclohexane	2	15	1	0	16
Methylcyclohexane	3	57	77	0	146
Methyleyclopentane	1	142	0	0	142
Chloroform[b]	72	206	364	0	1,000
Dibromochloromethane	72	207	363	0	1,000
Ethylbenzene	72	260	445	0	1,500
Methylene chloride	72	190	374	0	1,800
Tetrachloroethene	72	207	363	0	1,000
Toluene	72	2,232	4,282	0	15,000
Trichloroethene	72	209	362	0	1,000
Xylene (total)	72	1,459	2,491	0	7,600

a. Concentration of chemicals in groundwater are from Black and Veatch (1993).

b.	Compound	Fraction of total samples with "BJ" qualification flags (%)
	Acetone	22.22
	Chloroform	1.38

Table 4b. Descriptive statistics for metals detected in groundwater at the Panero site.

Compound	Number of samples	Arithmetic mean (µg/L)	Standard deviation (µg/L)	Minimum[a] (µg/L)	Maximum[a] (µg/L)
Antimony	47	5	13	0	40.000
Arsenic	47	2	6	0	40.000
Beryllium	47	0	0	0	2.000
Cadmium	47	0	1	0	3.000
Calcium	47	174,270	104,074	0	668000.000
Chromium	47	1	3	0	18.000
Copper	47	1	4	0	15.000
Iron	47	12,615	20,364	0	136000.000
Lead	47	1	2	0	8.000
Magnesium	47	63,332	37,145	0	241000.000
Manganese	47	4,498	5,642	0	21300.00
Mercury	47	0	0	0	0.000
Nickel	47	1	4	0	16.000
Potassium	47	10,078	13,865	0	10000.000
Selenium	47	1	2	0	6.000
Silver	47	1	3	0	12.000
Sodium	47	129,734	38,863	0	249000.000
Thallium	47	1	2	0	10.000
Zinc	47	10	31	0	174.000

a. Metal concentrations in groundwater are from Black and Veatch (1993).

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Figure 4. Isopleths of benzene concentration in groundwater at the Panero site in September 1992.

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1993 through March 1995 are provided in Figures A-19 through A-27 in Appendix A. The volume of JP-4 on the water table at OU 3 is currently estimated at 1.4E+06 gal.

Investigations to date indicate that the maximum depth at which groundwater contamination occurs is about 85 ft. Metals contamination in general has not proven to be a concern at the Panero site. All metal analytes are within the range of background levels both in soil and water, with the exception of manganese. The high manganese levels may be a result of the reducing environment by the presence of JP-4 in the subsurface. Oxygen levels in the subsurface in the area of highest fuel contamination are close to zero, probably due to oxygen consumption by hydrocarbon-metabolizing microbes.

Groundwater temperature in the shallow aquifer at OU 3 is approximately 75°F. The pH values for OU 3 groundwater range from 6.05 to 8.02. Concentrations of total dissolved solids (TDS) in groundwater at OU 3 range from 740 to 1,490 mg/L. Content of TDS in water samples from Box Springs Mutual Water Company, considered representative of background conditions, were approximately 400 mg/L.

General groundwater quality in the northern portion of Perris Valley, where OU 3 is located, and in the Moreno Valley is considered good. Concentrations of TDS in these valleys range from 250 to 1,000 mg/L. East of March AFB, values of TDS range from 400 to 500 mg/L. Concentrations of TDS in groundwater 1 mile northeast of March AFB range between 500 and 10,000 mg/L.

4. MATERIALS AND METHODS

The general approach for meeting the objectives identified in Section 2 is based on the *Technical Protocol for Implementing the Intrinsic Remediation with Long-Term Monitoring Option for Natural Attenuation of Dissolved-Phase Fuel Contamination in Ground Water (Draft)* (Wiedemeir et al. 1994). The materials and methods described in this section are derived from this source and others (Borden et al. 1995, Rifai et al. 1995, Chapelle et al. 1995). Methods described below utilize both qualitative and quantitative statistical methods to determine relationships between contaminants, electron acceptors, and nutrients in groundwater at OU 3.

Seven consecutive quarters of groundwater monitoring data are available for OU 3 wells in addition to a round of groundwater sampling from the September 1992 field investigation. These data sets vary somewhat in their completeness, analytes, and wells sampled. Quarterly groundwater monitoring originally included all base wells that were accessible and did not contain free-phase fuel, but the list has subsequently been abbreviated to only specific wells at the downgradient margins of each OU. Wells in the former tank farm area that are located in deep vaults requiring confined space entry to sample, contain dedicated fuel recovery pumps, or have free-phase fuel have not been included in quarterly sampling. Additionally, nitrate-nitrite and dissolved oxygen (DO) have not been consistently determined in quarterly sampling.

September 1992 data include sampling results for all wells installed during that field effort. These include the TF-, FP-, HP-, and CP- wells, as well as MW-06 through MW-25. Dissolved oxygen was not determined during sampling of these wells.

Analytes used in this study include water temperature, BTEX, TPH, DO, sulfate, nitrate-nitrite, dissolved iron (Fe), pH, TDS, total alkalinity, total hardness, bicarbonate, carbonate, o-xylene, and m+p-xylenes.

Methods used to meet each objective defined in Section 2 are described below.

Objective 1: Test the hypothesis that intrinsic bioattenuation occurs in groundwater at March AFB OU 3. Three tests are typically used to determine whether or not intrinsic bioattenuation occurs at significant rates in groundwater at a site (Rifai et al. 1995):

1. Decreases in contaminant concentrations

2. Decreases in electron acceptor concentrations

3. Increases in concentrations of byproducts.

This report includes one additional test, an analysis of variance (ANOVA) for electron acceptor concentrations in contaminated versus uncontaminated wells. This test determines whether or not there is a statistically significant relationship between the BTEX and electron acceptor values for a particular well. A statistically significant inverse relationship is evidence for intrinsic bioattenuation.

Objective 2: Test the hypothesis that intrinsic bioattenuation occurs in groundwater at March AFB OU 3 at rates and extents so that receptors will not be affected. This report includes estimates of rates of intrinsic bioattenuation, based on differences in contaminant concentrations between wells located along flowlines in the dissolved-phase plume and estimated travel times. Detailed fate and transport modeling will be performed using BIOPLUME III when the code becomes available later this year. BIOPLUME III provides significant advances over BIOPLUME II, including use of electron acceptors

other than oxygen, such as nitrate and sulfate, and the ability to input contaminant sources. Analytical calculations used to estimate time to reach background water quality in the aquifer, pending release of BIOPLUME III, are described in Section 4.2.

Objective 3: Test the hypothesis that intrinsic bioattenuation occurs at rates and extents so that the aquifer will eventually be restored to background water quality. This report includes discussion of the time required to restore the aquifer to background water quality by intrinsic bioattenuation.

4.1 Analysis of Existing Data

4.1.1 Microbial Studies

Several studies were performed during the OU 3 remedial investigation to determine microbial numbers and types and the ability of soil microorganisms native to soil at March AFB to biodegrade jet fuel. These are summarized below.

Utah State University 1991. This report was presented in Volume II, Appendix A of the feasibility study. This benchscale study determined biological activity of March AFB soil under simulated bioventing conditions. Soils collected from the Pritchard Fueling area at March AFB were determined to biodegrade weathered JP-4 at rates from 22 to approximately 100 mg JP-4 per kg soil per day. Nutrient addition was not found to significantly increase biodegradation rates.

U.S. Army Corps of Engineers 1992. The Army Corp of Engineers (ACOE) plated soil samples from split-spoon samples collected at OU 3 on nutrient agar. All soils analyzed had microbial populations between 10^4 and 10^6 colony-forming units per gram dry soil weight. These numbers are typical for soils with adequate organic matter and nutrients. In all samples, a substantial number of the microorganisms present had the ability to utilize one or more of the hydrocarbons tested. The presence of hydrocarbon-utilizing microorganisms in soil samples contaminated with JP-4 jet fuel suggests that native microorganisms have adapted to the presence of JP-4.

Idaho National Engineering Laboratory (INEL) 1993 (a). Microbial analyses were conducted on a biphasic sample of water and fuel that was collected from material bailed from well EX-02. The sample had a dull yellow layer of material at the fuel-water interface resembling algae. Subsamples were incubated aerobically and anaerobically. Rod-shaped gram-negative organisms ranging in length from 0.75 to 7 μm appeared on all agar plates. These microorganisms were tolerant of JP-4 but could not be determined to be actually degrading the fuel.

INEL 1993 (b). Field-scale bioventing testing indicated relatively low biodegradation rates in OU 3 soils. Relatively high pH and low nutrient values were believed to limit microbial activity in the locations tested.

4.1.2 Nutrient Analyses

Saturated and unsaturated zone soil samples recovered during split-spoon sampling in April 1994 were analyzed for Total Kjeldahl Nitrogen (TKN) and total and ortho phosphorus. Additionally, split-spoon samples were taken during installation of bioventing test wells in March 1993 and analyzed for total phosphorus and TKN.

4.1.3 Contaminant Distributions

Contaminant (BTEX) distributions are based on quarterly groundwater sampling data. Wells containing free-phase fuel or containing dedicated pumps, or located in belowgrade vaults have not been sampled since September 1992 (Quarter 2). BTEX concentrations in unsampled wells containing free-phase fuel, therefore, were assumed to be constant at September 1992 values.

4.1.4 Electron Acceptor Distributions

Similar to contaminant distribution data, electron acceptor distributions are based on quarterly groundwater sampling data, and the September 1992 data set. Wells containing free-phase fuel or containing dedicated pumps, or located in vaults have not been sampled since September 1992. Dissolved oxygen was not measured for the September 1992 sampling, and dissolved oxygen and nitrate-nitrite have not been consistently measured in subsequent quarterly sampling. All nitrate-nitrite is assumed to exist as nitrate because nitrite is metastable in the environment and is seldom present at significant concentrations (Wiedemeier et al. 1995).

Groundwater in uncontaminated zones immediately upgradient from OU 3 shows significant concentrations of electron acceptors. Dissolved oxygen concentrations for PANMW-12 range from 2.00 to 6.84 mg/L, with an average of 4.21 mg/L; sulfate ranges from 53,000–122,000 µg/L, with an average of 88,230; nitrate ranges from 13,900 to 25,000 µg/L, with an average of 20,420; and dissolved iron ranges from <10 to 37,400 µg/L.

A one-way ANOVA was performed for each electron acceptor between upgradient, uncontaminated wells screened in the shallow aquifer, and downgradient, contaminated wells. The purpose of the ANOVA was to test the hypothesis that DO, nitrate-nitrite, and sulfate concentrations in uncontaminated wells are significantly different than concentrations in contaminated groundwater. This is a statistically quantifiable test to determine, at the 95% confidence level, whether or not BTEX-contaminated water is depleted in electron acceptors relative to uncontaminated water. No significant loss processes for DO, nitrate-nitrite, and sulfate other than bioconversion are known to occur in groundwater. If concentrations of electron acceptors are significantly lower in contaminated groundwater than in uncontaminated groundwater, the difference is evidence that intrinsic biodegradation occurs in contaminated groundwater at OU 3. The hypothesis was tested at the 95% confidence level for each electron acceptor, using Scheffe's One-Way Analysis of Variance and the statistical software package STATGRAPHICS Plus (Manugistics, Inc. 1992). Monitoring wells PANMW-25 and PANMW-12 were used as upgradient, uncontaminated wells and monitoring wells PANFP-08 and PANMW-02 were used as downgradient, contaminated wells. All of these wells are screened in the shallow OU 3 aquifer. Wells PANFP-08 and MW-02 have the highest contaminant concentrations of any of the OU 3 wells sampled. All available quarterly sampling values for each well type (background versus contaminated) and electron acceptor type (DO, nitrate, and sulfate) were used as the sample populations. An F-ratio greater than one and a significance level less than 0.05 are regarded as statistically significantly different sample populations.

4.1.5 Byproduct Distributions

Byproduct distributions are based on quarterly groundwater sampling data and the September 1992 data set. Wells containing free-phase fuel or containing dedicated pumps, or located in vaults have not been sampled since September 1992. Potential byproducts identified in Table 1 include $HCO3^-$, H_2S, CH_4, and Fe^{+2}. Fe^{+2} is insoluble and, therefore, is not measured in groundwater sampling. H_2S and CH_4 are not measured in quarterly sampling at March AFB. $HCO3^-$, therefore, is the only reported biodegradation byproduct.

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A one-way ANOVA was performed for bicarbonate concentrations between upgradient, uncontaminated wells screened in the shallow aquifer and downgradient, contaminated wells. The purpose of the ANOVA was to test the hypothesis that bicarbonate concentrations in uncontaminated wells are significantly different than concentrations in contaminated groundwater. This is a statistically quantifiable test to determine, at the 95% confidence level, whether or not BTEX-contaminated water is enriched in a microbial byproduct of aerobic hydrocarbon respiration relative to uncontaminated water. If concentrations of bicarbonate are significantly higher in contaminated groundwater than in uncontaminated groundwater, the difference is regarded as proof that intrinsic biodegradation occurs in contaminated groundwater at OU 3. The hypothesis was tested at the 95% confidence level for each electron acceptor, using Scheffe's One-Way Analysis of Variance and the statistical software package STATGRAPHICS Plus (Manugistics, Inc., 1992). Monitoring wells PANMW-25 and PANMW-12 were used as upgradient, uncontaminated wells and monitoring wells PANFP-08 and PANMW-02 were used as downgradient, contaminated wells. All of these wells are screened in the shallow OU 3 aquifer. Wells PANFP-08 and MW-02 have the highest contaminant concentrations of any of the OU 3 wells sampled. All available quarterly sampling values for each well type (background versus contaminated) were used as the sample populations. An F-ratio greater than one and a significance level less than 0.05 are regarded as statistically significantly different sample populations.

4.1.6 Correlation of Contaminant and Electron Acceptor Distributions

4.1.6.1 Spatial Variations. Groundwater concentrations of contaminants and electron acceptors along a transect of OU 3 were plotted using September 1992 data. This is the only data set that included tank farm area wells. However, DO measurements were not made during this sampling effort. The transect was oriented in the direction of groundwater flow, identified in the 1993 ACOE report summarizing the 9/92 field work, and crossed the area of free-phase fuel and highest contaminant concentrations in the former tank farm area.

No DO concentrations were available for the 9/92 data set; therefore, average DO data for quarters 7 through 9 for wells MW-12, FP-03, and MW-07 and soil gas data from the tank farm area were used to infer DO concentrations with respect to contaminant concentrations. This transect is not based on an internally consistent data set and should be regarded only as qualitative evidence supporting or disproving intrinsic bioattenuation at OU 3. Oxygen concentrations measured at depths of 30 ft bgs during bioventing testing were approximately zero throughout the tank farm area in zones of soil contamination. It was inferred that DO concentrations in groundwater in wells containing fuel were likely zero also.

4.1.6.2 Temporal Variations. BTEX and electron acceptor concentrations were plotted for all wells without free product that showed measurable concentrations of BTEX, for the quarters the well was sampled. These plots show the temporal relationships between contaminant and electron acceptor concentrations for wells with contaminants. Background water quality for wells PANMW-12 and PANMW-25 was also plotted.

4.2 Estimating Rates of Contaminant Bioattenuation

Analytical calculations were used to estimate time to reach background water quality in the aquifer, pending release of BIOPLUME III. These calculations are based on observations of total BTEX reduction between wells located along the direction of groundwater flow at OU 3. This approach has been used by other researchers (see Table 7). Well PANTF-07, which contains free-phase fuel, is used as a contaminant source. The total BTEX concentration measured in groundwater samples from PANTF-07 in September 1992 was 44,000 μg/L. Well PANFP-03, located 308 ft directly downgradient from PANTF-07, contained less than 10 μg/L total BTEX. Using a mean groundwater velocity of 33 ft/yr, travel time from well TF-07 to MW-07 is 9.33 years. Assuming first-order kinetics, an apparent loss rate constant, which accounts for

all loss processes including biodegradation, dilution, dispersion, adsorption, and volatilization, a rate constant can be calculated as

$$\frac{\ln(\frac{C}{C_0})}{t} = -k \qquad (1)$$

where

C = total BTEX concentration at downgradient well = <10 µg/L

C_0 = total BTEX concentration at upgradient (source) well = 44,000 µg/L

t = travel time

= distance/groundwater velocity = 9.33 years.

A value for k of 0.8992 year^{-1} is obtained by this method. A half-life for total BTEX can be calculated as

$$\frac{\ln(0.5)}{-k} = t_{1/2} \qquad (2)$$

A half-life of 0.77 years for total BTEX is obtained by this method.

5. RESULTS

5.1 Analysis of Existing Data

5.1.1 Site Conditions

The relatively high groundwater temperature (75°F) is conducive to microbial activity. The pH range in OU 3 groundwater, 6.4 to 8.0, lies within the ideal range for microbial growth of 6.5 to 8.5. Alkalinity is fairly high, which provides for buffering of pH changes caused by microbial metabolism of BTEX.

5.1.2 Microbial Studies

Results of the microbial studies performed on March AFB OU 3 soils indicate that microbes exist at levels ranging from 10^4 to 10^6 cfu/g, which are representative levels for typical soils. No evidence of inhibition by the presence of petroleum contamination exists. On the contrary, the INEL study found bacteria at the fuel-water interface tolerant of JP-4, and perhaps metabolizing the fuel, which suggests that microorganisms are exploiting the petroleum contamination as a food source. Further evidence of fuel-degrading bacteria is provided by the ACOE study, which identified fuel-degrading bacteria in unsaturated zone soils. These studies indicate that fuel-degrading bacteria exist in soil and groundwater at March AFB OU 3.

5.1.3 Nutrient Analyses

Soils at OU 3 are generally deficient in nitrogen and phosphorus. Low nutrient levels may limit the rate and extent of biodegradation in some areas. The total nitrogen content of soils typically ranges from <0.02% (200 mg/kg) in subsoils to >2.5% (25,000 mg/kg) in peats, and the surface layer of most cultivated soils contains 0.06 % (600 mg/kg) to 0.5% (5,000 mg/kg) total nitrogen (Page et al. 1992).

March AFB OU 3 soil TKN values determined from split-spoon sampling during well installation in April 1994 ranged from U-flagged values near 24 mg/kg to 76.2 mg/kg. Total phosphorus values are also low, ranging from 1.41 mg/kg to 6.77 mg/kg.

March AFB OU 3 unsaturated zone soil TKN values determined from split-spoon sampling during bioventing test well installation in April 1994 ranged from nondetect to 110 mg/kg. Therefore, these soils are nitrogen deficient. Total phosphorus concentrations ranged from 176 mg/kg to 809 mg/kg. Therefore, these soils are not deficient in phosphorus.

Nitrogen and phosphorus are required by microbes for cell-building. Ideal hydrocarbon-to-nitrogen-to-phosphorus ratios are often cited as 100:10:1 to 200:10:1 (Sims et al. 1986). Using these ratios and the maximum nitrogen and phosphorus levels cited above, the maximum concentration of biodegradable hydrocarbon in soil at OU 3 would range from 240 mg/kg to 760 mg/kg with respect to nitrogen and 141 to 677 mg/kg with respect to phosphorus.

5.1.4 Contaminant Distributions

Four wells at OU 3 that previously contained measurable BTEX concentrations now show nondetectable concentrations of these compounds. These include wells PANMW-02, PANHP-04, PANMW-08, and PANCP-08. Initial concentrations of benzene in these wells of up to 26 ppb have declined to nondetect in 3 years. All of these wells are located in the dissolved-phase zone of

contamination. One originally uncontaminated well, CP-08, showed benzene concentrations of 4.00 µg/L and 18.0 µg/L in quarters 5 and 6, respectively, but concentrations have since returned to nondetect.

All other wells located in the dissolved-phase zone of contamination show declining BTEX concentrations. Figures 5 through 8 show BTEX concentrations versus time for wells PANMW-13, PANMW-02, PANFP-08, and PANHP-04, respectively.

The apparent extent of free product on the water table increased during the period 1992 to 1995, as seen in Figures A-19 through A-27. BTEX concentrations in wells with fuel are assumed constant at 1992 (maximum) values; therefore, the apparent extent of the dissolved-phase plume has also increased. However, significant migration of dissolved phase contaminants beyond the area of free product has not occurred. Figures A-30 through A-57 show BTEX concentrations measured in OU 3 monitoring wells from 12/92 (Quarter 3) through 6/94 (Quarter 9). Dissolved-phase BTEX distributions can be seen in general to follow the distribution of free product and do not appear to migrate significant distances beyond the margins of the free product. Dissolved and free-phase contamination in MW-02 has disappeared. The 10 ppb benzene isopleths in Figures A-30 through A-36 can be seen to advance and contract in the downgradient direction (southeast) toward wells PANHP-11 and PANCP-11, but to date these wells remain uncontaminated.

5.1.5 Electron Acceptor Distributions

Groundwater in uncontaminated zones immediately upgradient from OU 3 shows significant concentrations of electron acceptors. Dissolved oxygen concentrations for PANMW-12 range from 2.00 to 6.84 mg/L, with an average of 4.21 mg/L; sulfate ranges from 53,000 to 122,000 µg/L, with an average of 88,230; nitrate ranges from 13,900 to 25,000 µg/L, with an average of 20,420; and dissolved iron ranges from <10 to 37,400 µg/L.

Electron acceptor concentrations and theoretical BTEX biodegradation potential are tabulated in Table 5. The theoretical biodegradation potential is based on the stoichiometry shown in Table 1.

The total of 24,280 µg/L BTEX theoretical biodegradation assumes that the stoichiometry shown in Table 5 is correct, that all three processes occur, and that other conditions, such as nutrient availability, are not limiting. The total value represents the BTEX concentration in groundwater that theoretically could be completely biodegraded using the background electron acceptor concentrations in uncontaminated groundwater at OU 3. The fact that this water moves into OU 3 at the same rate that contaminated water moves out indicates that biodegradation will significantly remove contaminants. The highest total BTEX concentration observed in OU 3 groundwater to date was 35,000 µg/L in well TF-05 in September 1992, which contained free product. The highest total BTEX concentration observed in quarterly sampling of wells without free product was 11,340 µg/L. In situ biodegradation using naturally occurring electron acceptors is theoretically capable of removing all of the dissolved-phase BTEX found in wells without free-phase fuel and approximately 70% of the total BTEX in wells with fuel.

Analysis of variance. The ANOVA results for contaminated and uncontaminated wells are tabulated in Table 6. Plots of the means and 95% confidence intervals for each electron acceptor in uncontaminated and contaminated wells are provided in Figures 9 through 11. An F-ratio greater than one, and a significance level less than 0.05 are regarded as statistically significantly different sample populations. The results reported in Table 6, therefore, indicate that electron acceptor concentrations are significantly different between contaminated and uncontaminated wells. This is evidence that significantly higher levels of aerobic and anaerobic microbial respiration have occurred in contaminated water, relative to uncontaminated water, at the 95% confidence level.
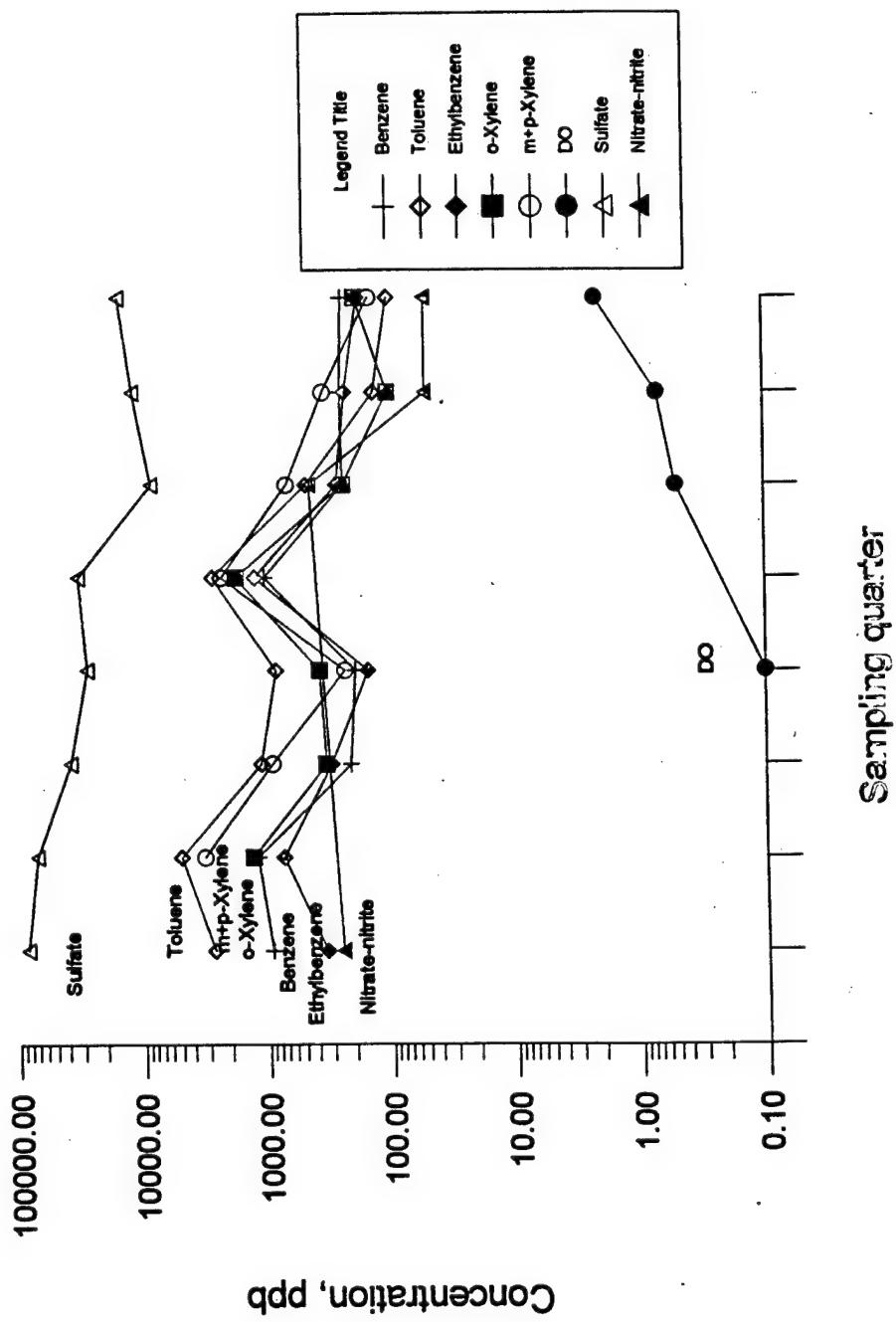
Figure 5. Concentrations of BTEX and electron acceptors for quarters 1–9 for well PANFP-08.
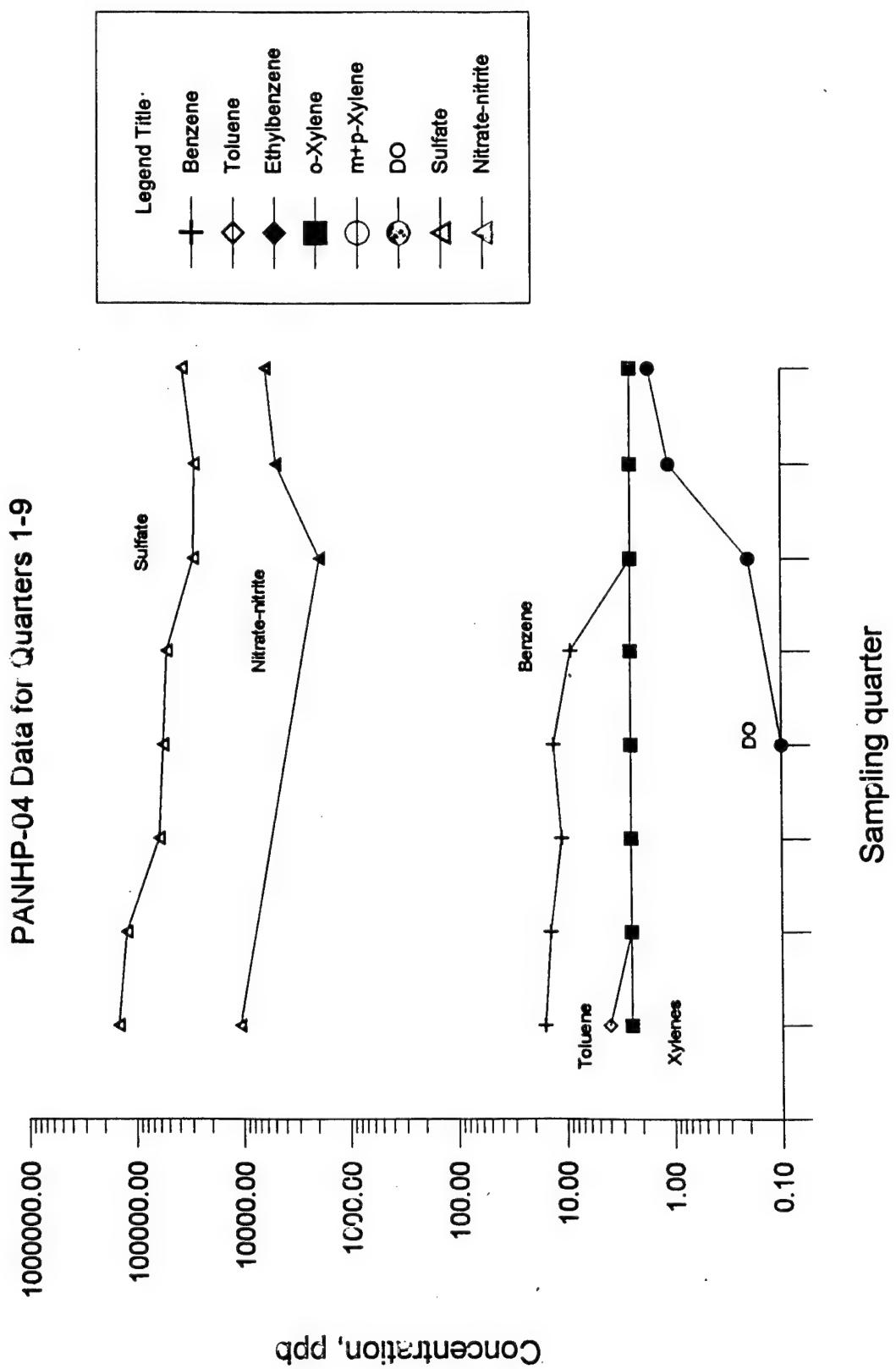
Figure 6. Concentrations of BTEX and electron acceptors for quarters 1–9 for well PANHP-04.

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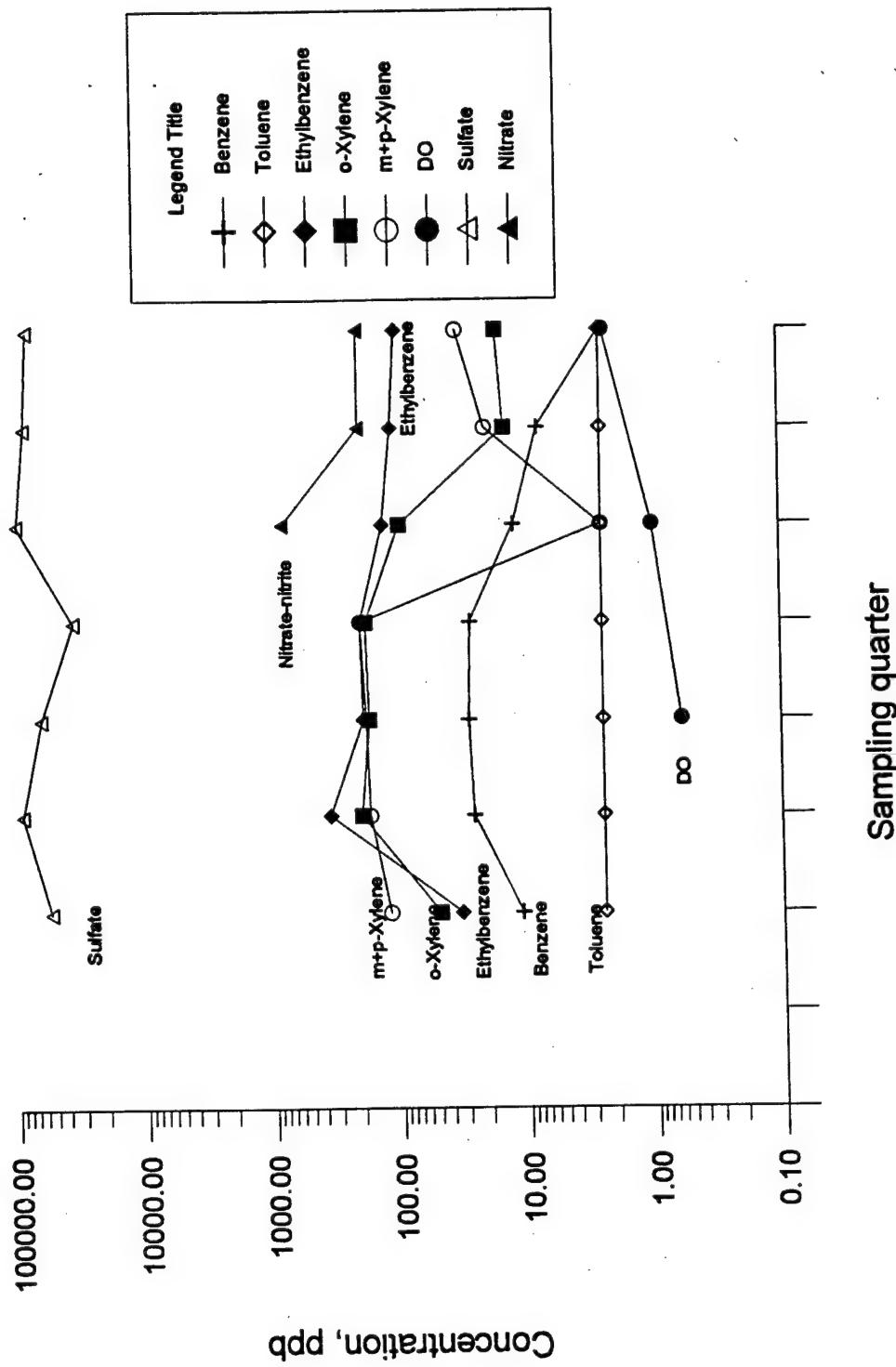
Figure 7. Concentrations of BTEX and electron acceptors for quarters 1–9 for well PANMW-02.
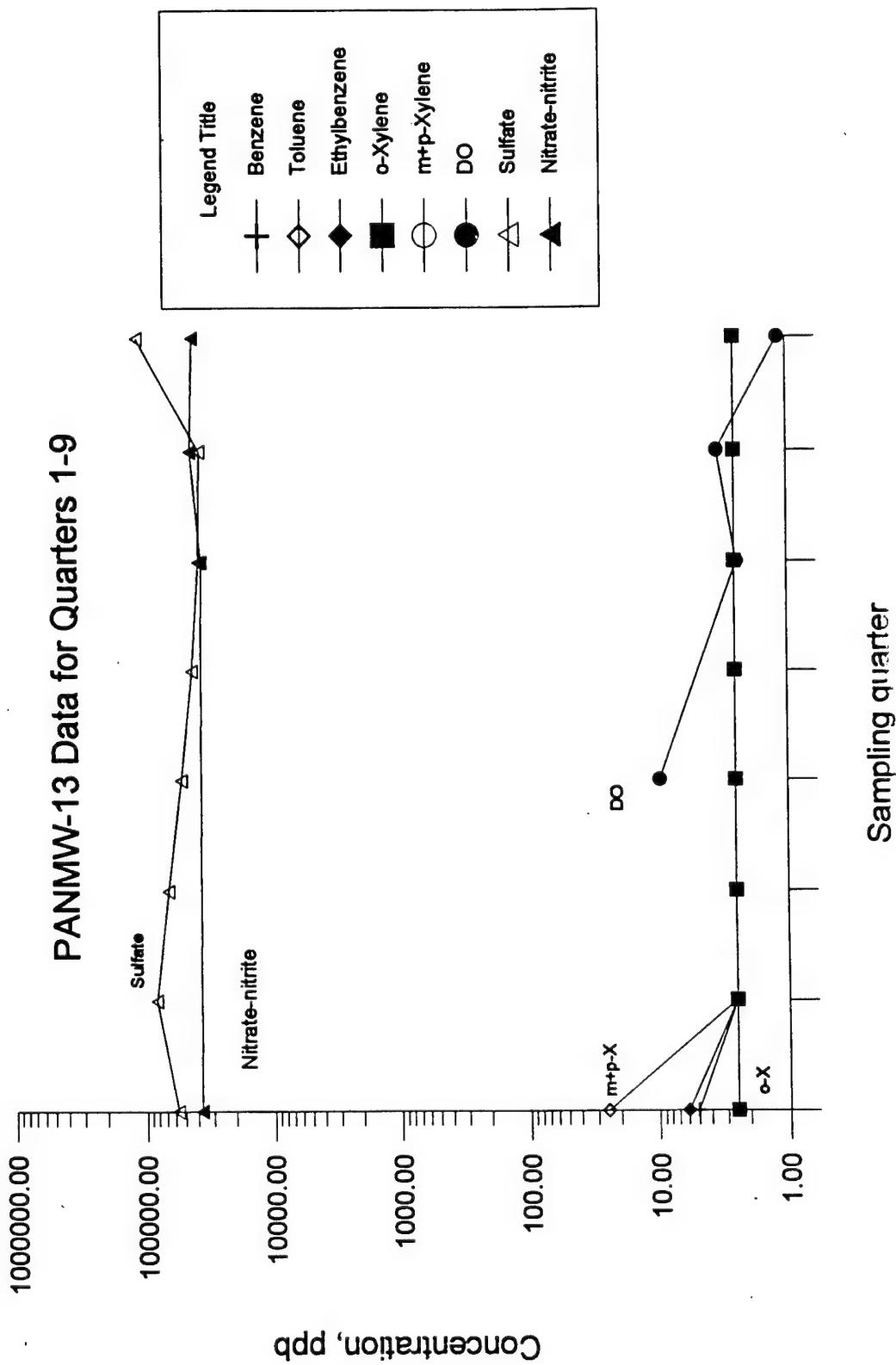
Figure 8. Concentrations of BTEX and electron acceptors for quarters 1–9 for well PANMW-13.

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Table 5. Average electron acceptor concentrations and theoretical BTEX biodegradation potential.

Electron acceptor	Average concentration in PANMW-12, µg/L	Theoretical electron acceptor to BTEX requirement	Theoretical BTEX biodegradation potential
Oxygen	4,210	3.14:1	1,341
Nitrate	20,420	4.9:1	4,167
Sulfate	88,230	4.7:1	18,772
Total	NA[a]	NA	**24,280**

a. Not applicable.

Table 6. ANOVA results for test of significance in electron acceptor concentrations between background and contaminated wells.

Electron acceptor	F-ratio	Significance level
Dissolved oxygen	30.095	0.0001
Nitrate	150.771	0.0000
Sulfate	10.826	0.0027

95 % Scheffe

Intervals for Factor Means
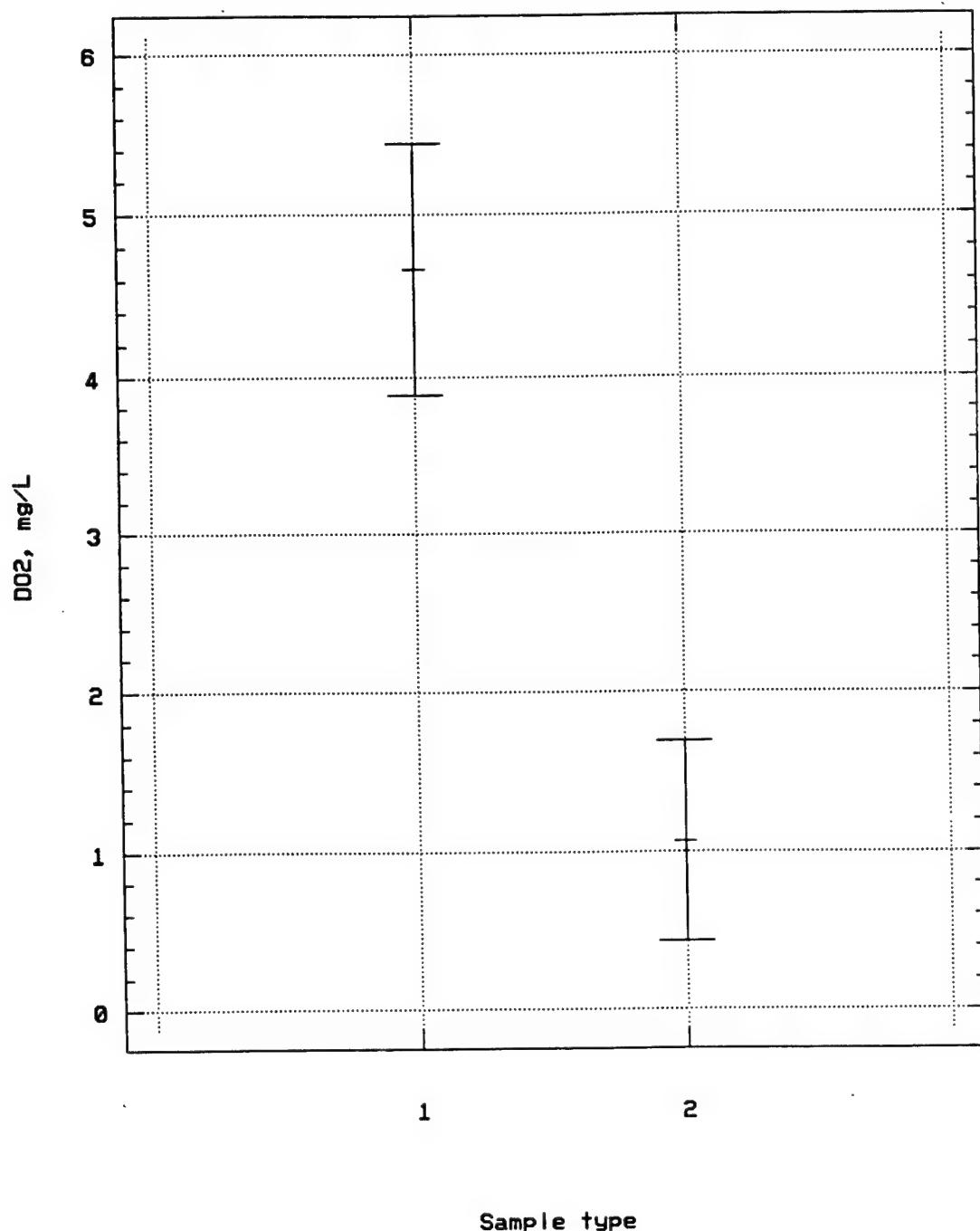
**Figure 9.** Mean and 95% confidence interval for DO in clean versus contaminated wells at OU 3 (1 = clean, 2 = contaminated).

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Figure 10. Mean and 95% confidence interval for nitrate in clean versus contaminated wells at OU 3 (1 = clean, 2 = contaminated).

95 % Scheffe

Intervals for Factor Means
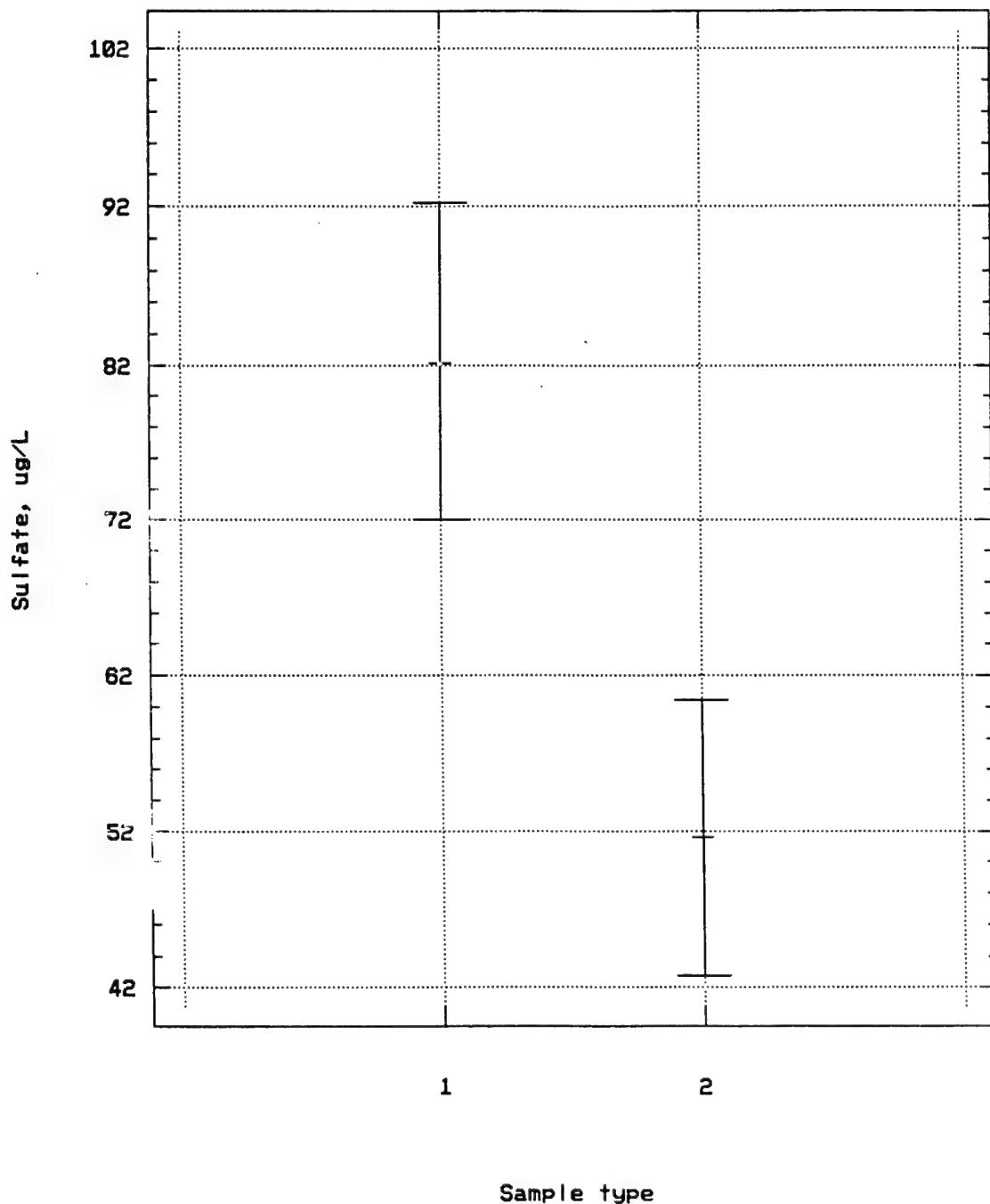
Figure 11. Mean and 95% confidence interval for sulfate in clean versus contaminated wells at OU 3 (1 = clean, 2 = contaminated).

5.1.6 Byproduct Distributions

No byproducts were measured in the November 1992 groundwater sampling and, therefore, are not included in the transect results. Bicarbonate concentrations in individual wells measured in quarterly monitoring do not show any clear trends. However, the ANOVA results for comparison of bicarbonate concentrations between contaminated versus uncontaminated wells show a statistically significant difference. The F-ratio for this test was 63.06, and the significance level was 0.0000. The means and 95% confidence intervals for bicarbonate concentrations for uncontaminated and contaminated wells are plotted in Figure 12. An F-ratio greater than one and a significance level less than 0.05 are regarded as statistically significantly different sample populations. These results, therefore, indicate that bicarbonate concentrations are significantly different between contaminated versus uncontaminated wells at the 95% confidence level. This is further evidence that increased levels of aerobic biodegradation have occurred in the fuel-contaminated water, relative to uncontaminated water.

5.1.7 Correlation of Contaminant and Electron Acceptor Distributions

Figure 13 shows BTEX and electron acceptor concentrations along a transect across OU 3. Figure A-16 shows locations of wells used for the transect. The upgradient well, PANMW-12, showed ignominiously high concentrations of dissolved iron but was otherwise representative of background water quality. As the transect approaches the former tank farm area, BTEX concentrations increase and nitrate-nitrite and iron concentrations drop. Sulfate is relatively unchanged at well PANFP-05. One interpretation of these data is that nitrate is being used preferentially to sulfate in anaerobic respiration, which is consistent with other researcher's data indicating the same order of utilization. As nitrate-nitrite is more rapidly depleted between wells FP-05 and TF-08, sulfate depletion can also be seen. As the center of the plume is reached, BTEX concentrations at well TF-07 rise to a maximum of over 44,000 ppb and nitrate is not present at measurable concentrations—the value of 10 ppb seen on the plot is the detection limit. After well TF-08, nitrate-nitrite and sulfate concentrations rise as BTEX concentrations fall.

Dissolved iron concentrations along the transect are representative of Fe^{+3} reduction to insoluble Fe^{+3}, except for the initial high value in the upgradient well (MW-12). Dissolved iron concentrations drop initially, then rise as the center of the tank farm area is approached, then decline again as the periphery of the dissolved contaminant plume is approached.

Contaminant-electron acceptor relationships with respect to time are shown graphically in Figures 5 through 8 for wells PANFP-08, PANHP-04, PANMW-2, and PANMW-13. Most of these plots qualitatively show an inverse relationship between contaminant and electron acceptor concentrations indicative of ongoing biodegradation.

5.2 Estimating Rates of Contaminant Bioattenuation

A value for k of 0.8992 year^{-1} and a half-life of 0.77 years for total BTEX were estimated using first-order kinetics. This method of estimating rate constants and half-lives is conservative because the BTEX concentrations in well PANFP-03 were below detection limits and, therefore, the detection limits were used as concentrations in the well. Actual concentrations are less than the detection limit. The actual rate constant is larger, and the actual half-life is smaller. Similar calculations can be made for benzene, with an initial concentration in the upgradient well of 9,300 µg/L and using the benzene detection limit of 2.5 µg/L as the concentration in the downgradient well. The benzene apparent loss rate constant and half-life obtained by this method are 0.8809 year^{-1} and 0.7867 years, respectively.

95 % Scheffe

Intervals for Factor Means

(X 10000)
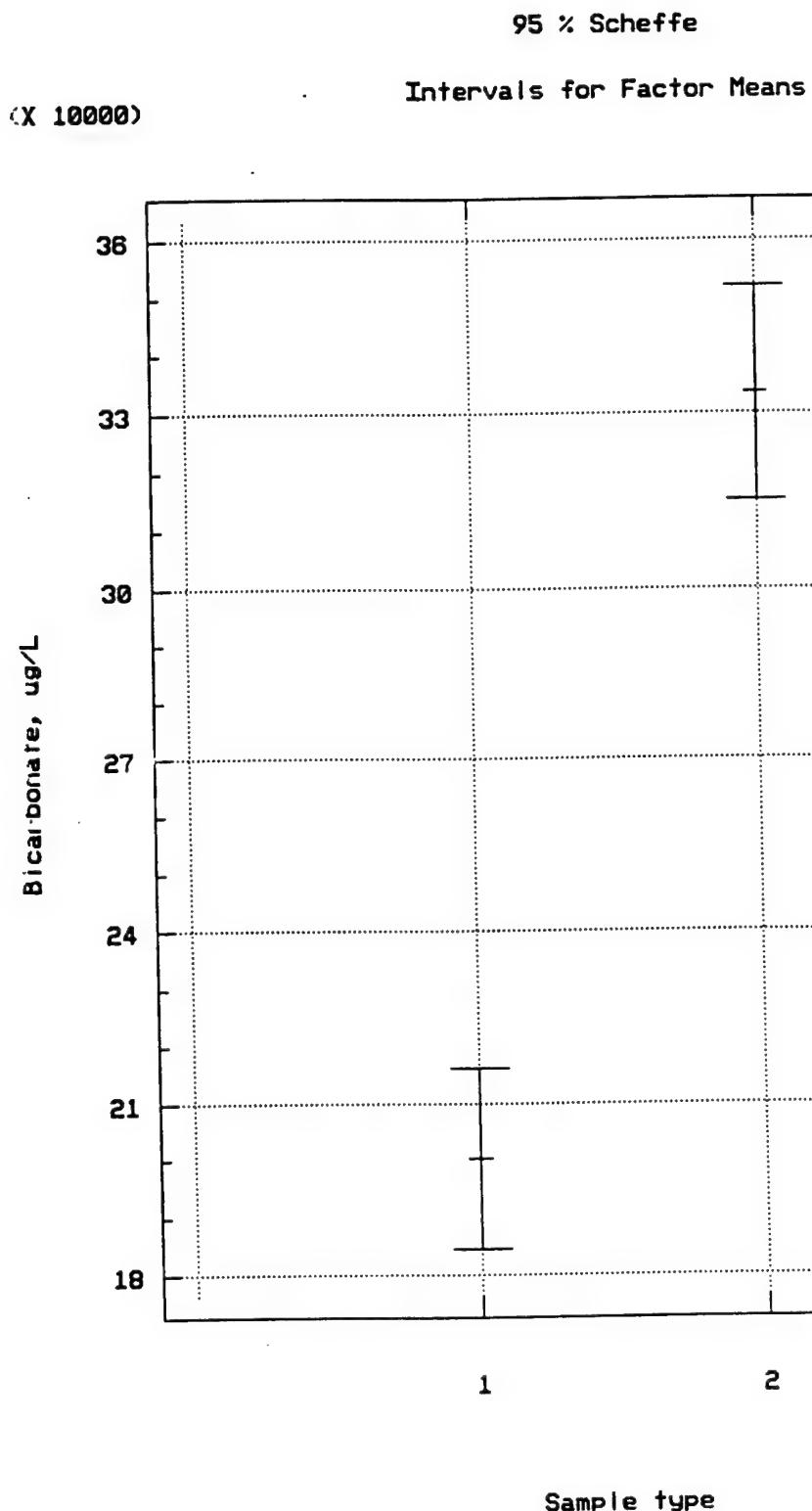
Figure 12. Mean and 95% confidence interval for bicarbonate in clean versus contaminated wells at OU 3 (1 = clean, 2 = contaminated).
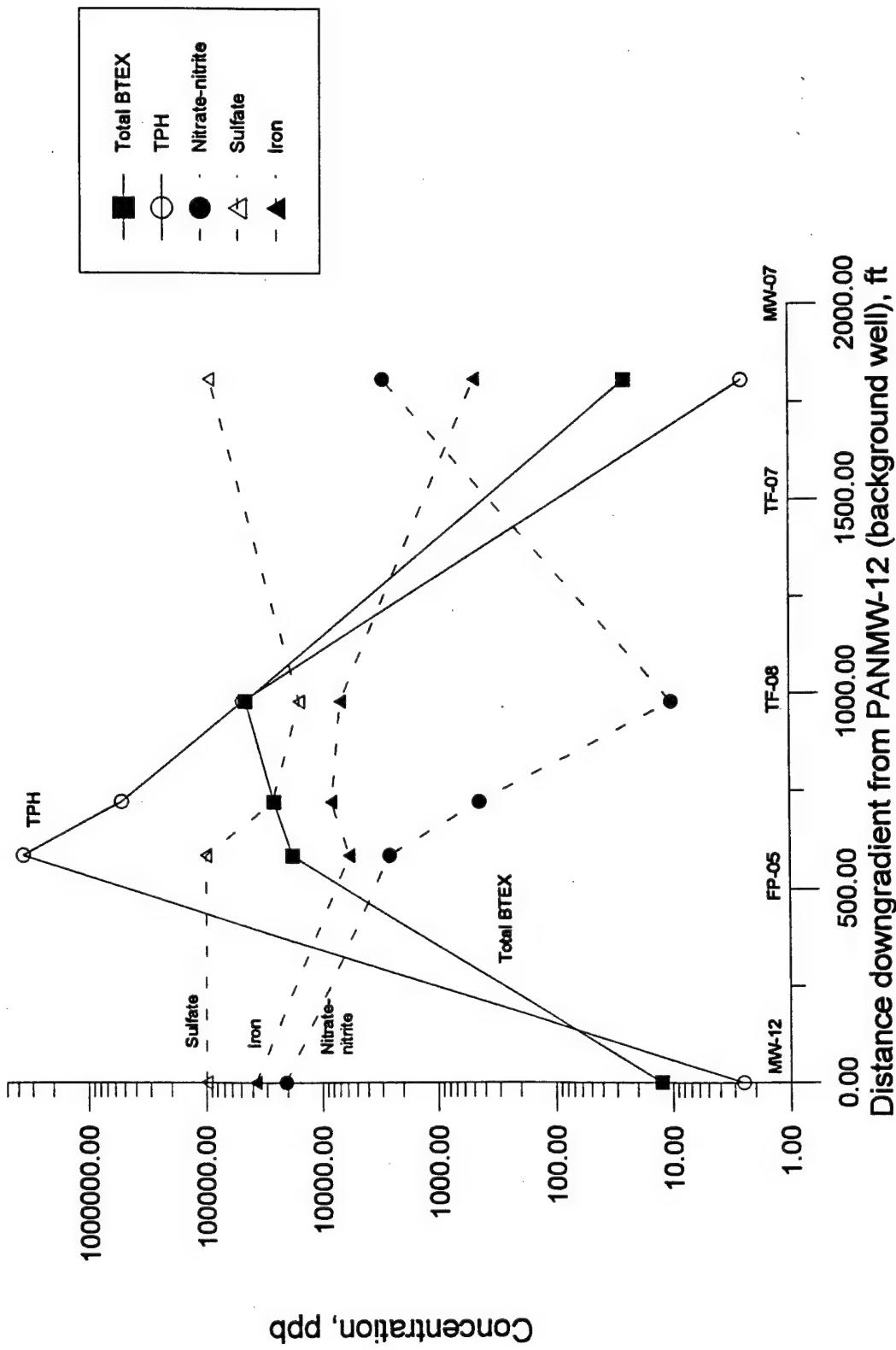
Figure 13. BTEX and electron acceptor concentrations for wells located along OU 3 transect.

This method estimates apparent loss rate constants, not biodegradation rates. Biodegradation rates cannot be effectively measured using existing data, because concentrations of recalcitrant organics such as trimethylbenzene have not been measured. Isomers of this compound are adsorbed, volatilize, and otherwise behave like benzene in groundwater but are not significantly aerobically biodegraded. Trimethylbenzene has been used by others (Wiedemeir et al. 1995) as an internal standard, and BTEX concentrations downgradient of a source were normalized to trimethylbenzene concentrations to determine loss due to biodegradation alone.

These apparent loss rate constants can be used to estimate benzene and total BTEX concentrations in groundwater at the downgradient end of OU 3, and the distance downgradient from the source where BTEX concentrations reach risk-based clean-up objectives defined in the OU 3 feasibility study. Equation (3) can be used to estimate travel time in the aquifer required to reach the risk-based clean-up level for benzene of 0.3 µg/L as follows:

$$v \times \frac{\ln \frac{C}{C_0}}{-k} = d \tag{3}$$

where

v = groundwater velocity = 33 ft/yr

C = benzene preliminary remediation goal (PRG) = 0.3 µg/L

d = travel distance from source required to reach PRG

C_0 = maximum benzene concentration in tank farm area

= 9,300 µg/L in well TF-07 in September 1992.

The estimated downgradient distance from the contaminant source area where the benzene PRG will be attained by natural attenuation and biodegradation is 387 ft. This is well within the confines of the OU.

6. DISCUSSION

Hypothesis 1 is accepted, based on the results of the ANOVA of electron acceptor concentrations in contaminated versus clean wells. ANOVA results indicate that intrinsic biodegradation occurs in OU 3 groundwater, using oxygen, nitrate and sulfate as electron acceptors. The ANOVA results further indicate that, based on the magnitude of the F-ratio, oxygen and nitrate-nitrite concentrations are most strongly correlated indicating that these electron acceptors are used to a greater extent than sulfate. These results are consistent with other researcher's observations (Rifai et al. 1995). Examination of background water quality shows concentrations of electron acceptors more than adequate to biodegrade dissolved phase contaminants before they migrate far from the source in the tank farm area.

Visual examination of plots of electron acceptors and BTEX versus time for individual wells generally shows declining BTEX concentrations and increasing electron acceptor concentrations over time. These trends are further evidence supporting acceptance of Hypothesis 1.

Hypothesis 2 is accepted, based on estimates of BTEX apparent loss rates and half-life. BTEX will not migrate outside the confines of OU 3 or outside the former tank farm area under current conditions. A rising water table will continue to create residual saturation below the water table, further increasing the size of the groundwater source area, but intrinsic bioattenuation is capable of containing the dissolved plume near the tank farm area as long as electron acceptor concentrations in groundwater remain at current levels.

The estimate of BTEX apparent loss rate obtained from observations of BTEX concentrations in OU 3 wells is in good agreement with those obtained in BIOPLUME III modeling by Rifai et al. (1995) and with those reported by other researchers in field investigations. These results are shown in Table 7.

Nutrient deficiencies may limit the extent of contaminant biodegradation in areas of high hydrocarbon concentrations at OU 3. However, nutrients appear not to limit the rate and extent of biodegradation of hydrocarbons in the dissolved-phase BTEX plume at OU 3, relative to the other studies reported on Table 7.

Hypothesis 3 cannot be accepted with the data available. Microorganisms are not capable of metabolism of significant quantities of nonaqueous phase petroleum hydrocarbons (Mihelcic et al. 1995); therefore, no biodegradation of the free-phase floating fuel and residual saturation is expected. The time for complete restoration of the aquifer to background water quality without active restoration is unknown.

Table 7. Comparison of benzene and total BTEX apparent loss and biodegradation rates in field and modeling studies.

Study	First-order BTEX apparent loss rate (per day)	First-order benzene apparent loss rate (per day)	Type of study
INEL (this paper)	2.46E-03	2.41E-03	Apparent loss rates obtained from field observations of concentrations versus travel time at March AFB, CA; groundwater velocity = 33 ft/yr = 2.97E-02 m/d
Rifai et al. (1995)	Ranged from -2.1E-05 to -1.3E-01	NA[a]	BIOPLUME III results for apparent loss at 6 mg/L O_2; lower value is for a silty aquifer with low hydraulic gradient, higher value is for a sandy aquifer with a high hydraulic gradient
Kemblowski et al. 1987[b]	NA	3.5E-03	Apparent loss measured at Morgan Hill, CA, groundwater velocity = 5E-02 m/d
Wiedemeier et al. 1994[b]	NA	3.0E-02 to 9.0E-02	Biodegradation rates obtained from field observations of concentrations versus travel time at Hill AFB, normalized to trimethylbenzene as internal standard. Groundwater velocity = 0.5 m/d
Ibid[b]	NA	0.0 to 4.0E-03	Biodegradation rates obtained from field observations of concentrations versus travel time at Patrick AFB, normalized to trimethylbenzene as internal standard; groundwater velocity = 0.13 m/d
Buscheck et al. 1993[b]	NA	5.5E-04	Apparent loss rates obtained from field observations of concentrations versus travel time at Fairfax, VA. Groundwater velocity = 0.015 m/d
Wilson et al. 1990[b]	NA	2.0E-03	Apparent loss rates obtained from field observations of concentrations versus travel time at Traverse City, MI; groundwater velocity = 1.5 m/d
Dupont et al. 1994[b]	5.0E-03	NA	Rates from mass balance on field observations

a. NA = data not available.

b. As reported in Rifai et al. (1995).

7. SUMMARY AND CONCLUSIONS

The data presented and discussed in this report support the following conclusions:

1. Intrinsic bioattenuation of dissolved-phase JP-4 jet fuel constituents occurs in groundwater at March AFB OU 3, at significant rates and extents. Aerobic biodegradation is the dominant intrinsic bioattenuation at the site, based on high electron acceptor concentrations and low groundwater velocities. Electron acceptors and biodegradation byproducts show statistically significant inverse relationships between samples from contaminated and uncontaminated wells.

2. Intrinsic bioattenuation occurs in groundwater at March AFB OU 3 at rates and extents so that receptors will not be affected. Estimated apparent loss rates for benzene show that the groundwater PRG for benzene is attained within 387 ft of the contaminant source. The nearest receptor is approximately 1 mile away from the source. Therefore, no receptors are affected.

3. Intrinsic bioattenuation does not occur at rates and extents so that the entire aquifer will eventually be restored to background water quality. Little or no biodegradation of free-phase floating fuel or residual saturation is expected; therefore, concentration of BTEX in groundwater in the tank farm area are likely to remain above PRGs for the indefinite future. Within 300–400 ft of the outer boundaries of the free-phase fuel, BTEX concentrations should remain constant at less than PRGs for the indefinite future.

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Appendix A

Contaminant Distributions
at Operable Unit 3
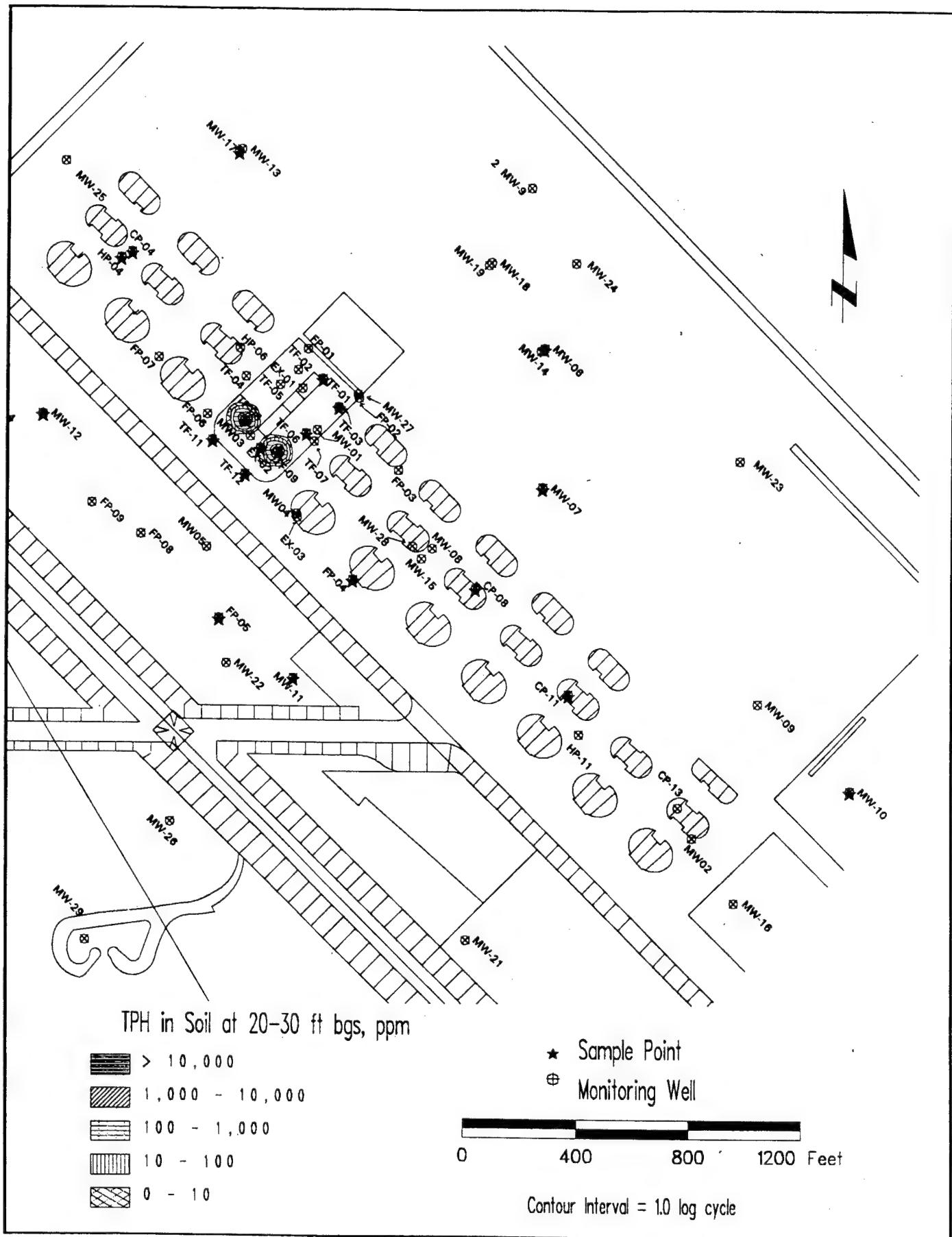
Figure A-1. Isopleths of total petroleum hydrocarbon contamination in soils at 20 to 30 ft deep at the Panero site.

Figure A-2. Isopleths of total petroleum hydrocarbon contamination in soils at 30 to 40 ft deep at the Panero site.
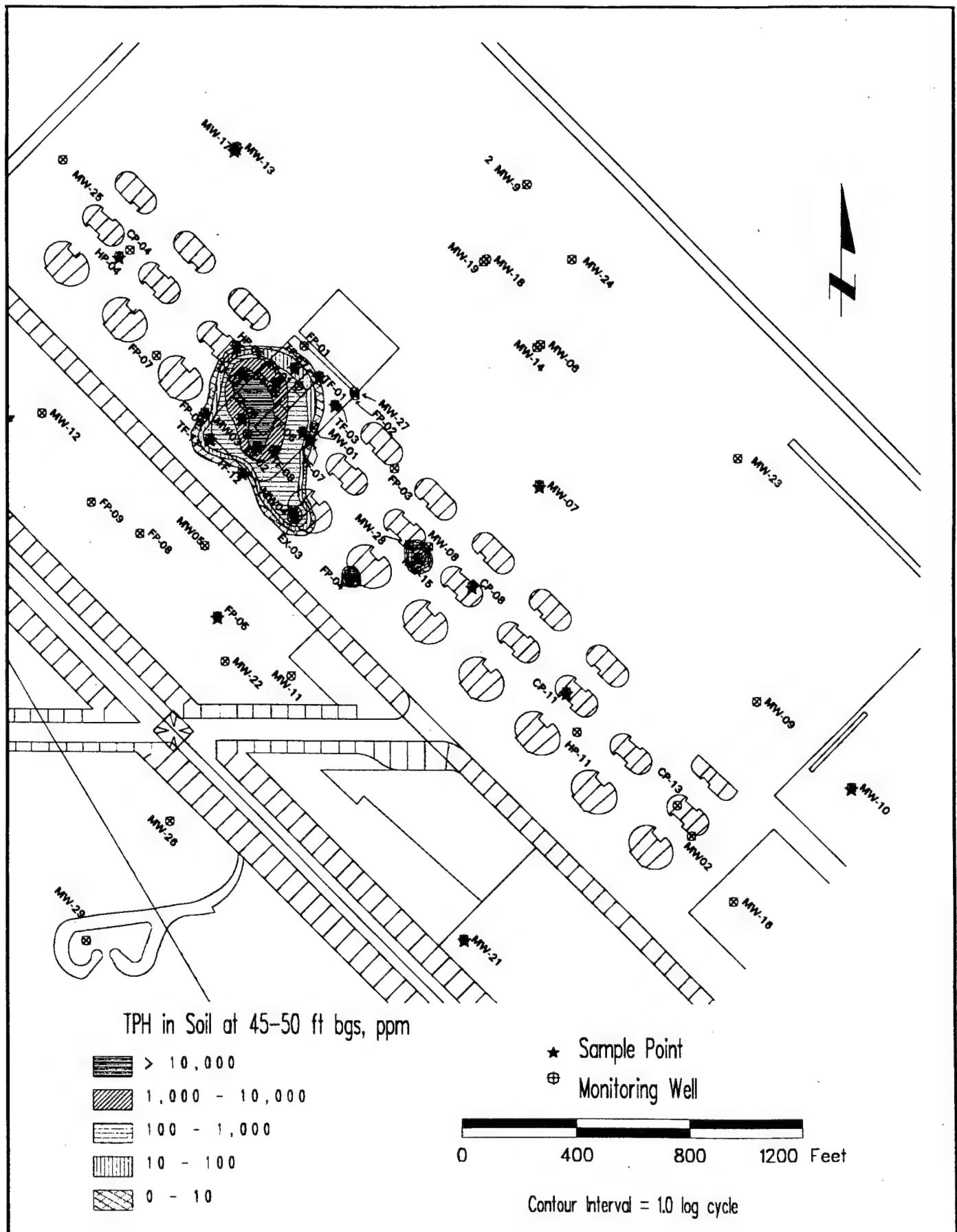
Figure A-3. Total petroleum hydrocarbons contamination in soil at 20 to 30 ft deep at the Panero site.

Figure A-4. Benzene contamination in soil at 20 to 30 ft deep at the Panero site.

A-6

Figure A-5. Benzene contamination in soil at 30 to 40 ft deep at the Panero site.
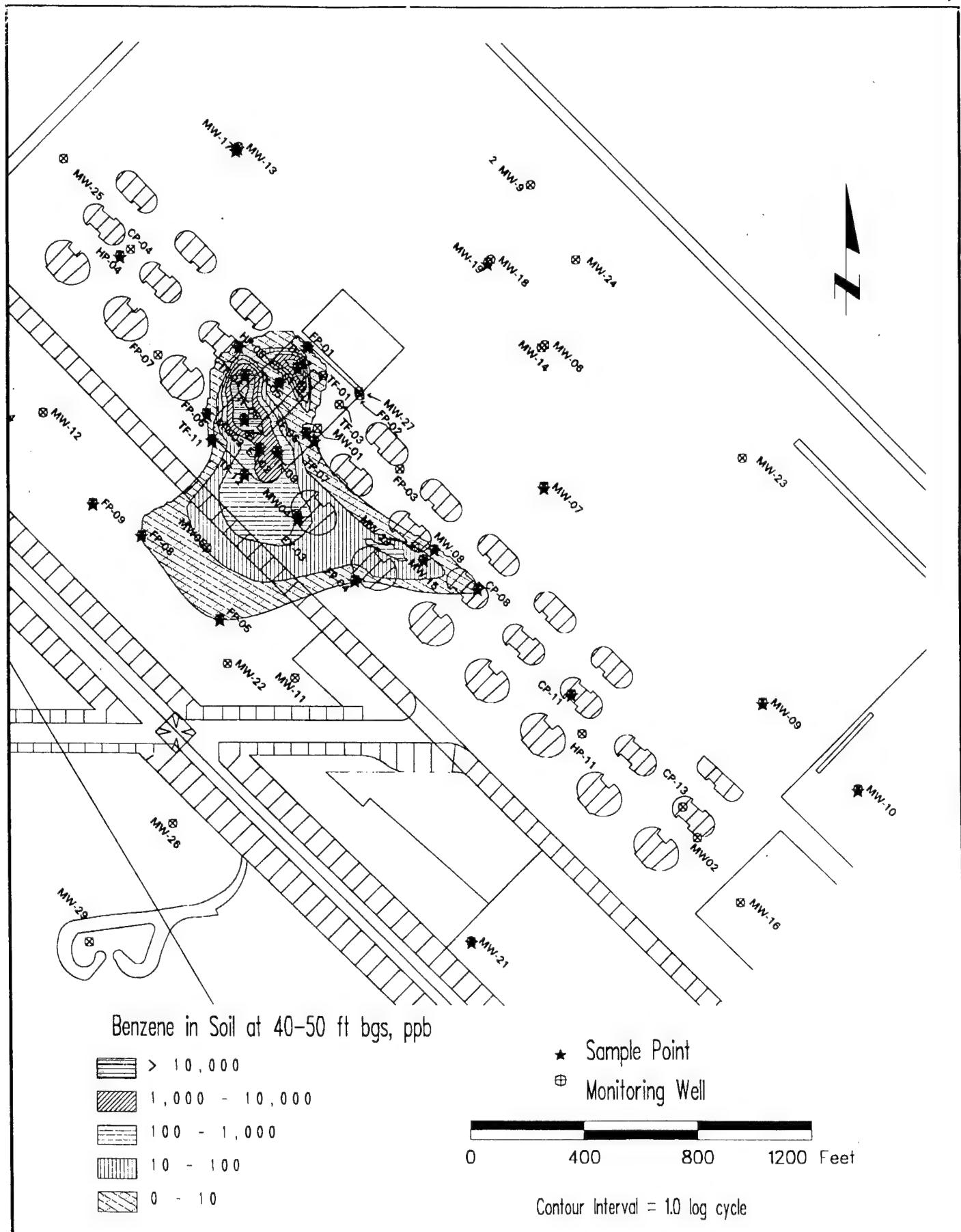
Figure A-6. Benzene contamination in soil at 40 to 50 ft deep at the Panero site.
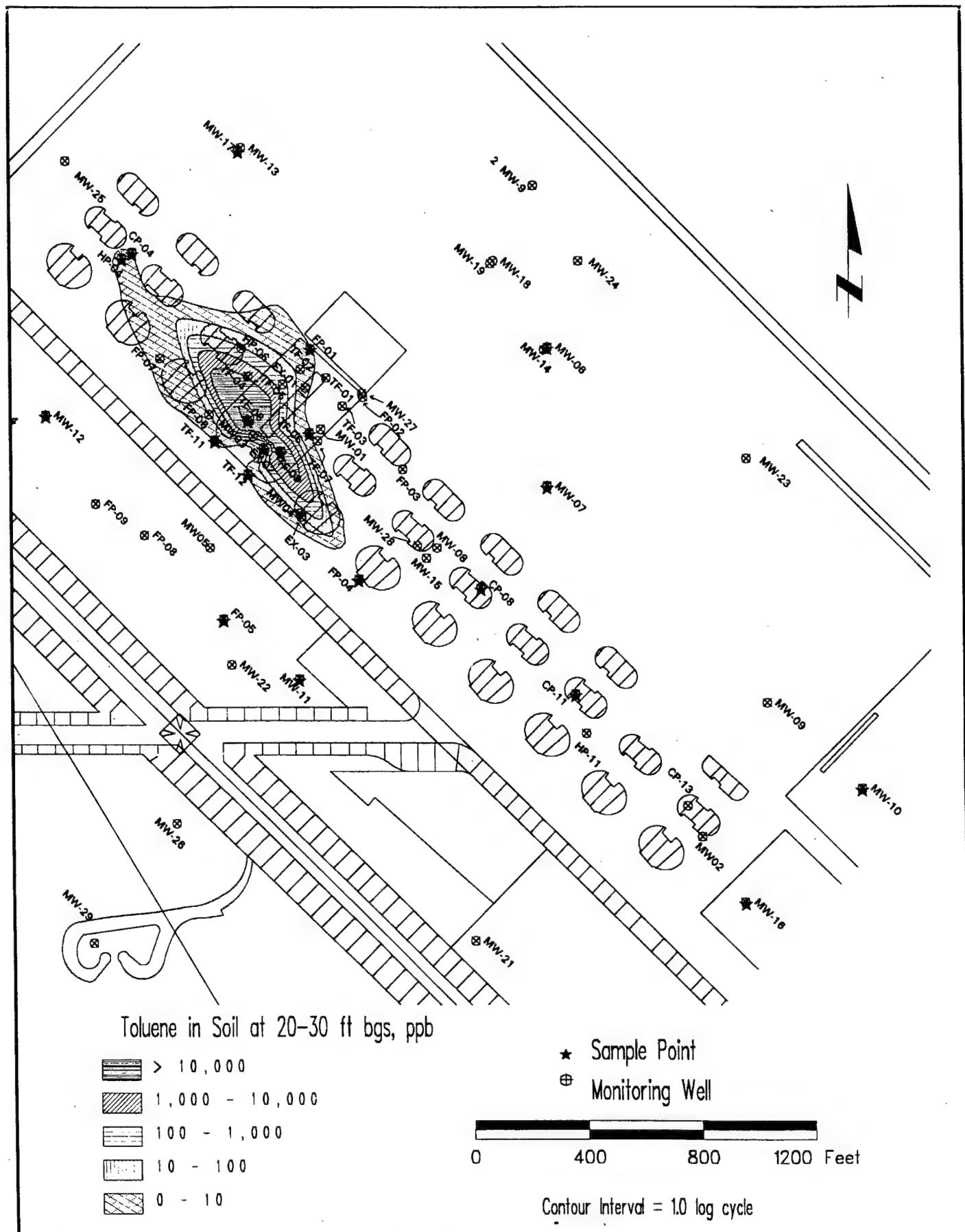
Figure A-7. Toluene contamination in soil at 20 to 30 ft deep at the Panero site.

Figure A-8. Toluene contamination in soil at 30 to 40 ft deep at the Panero site.
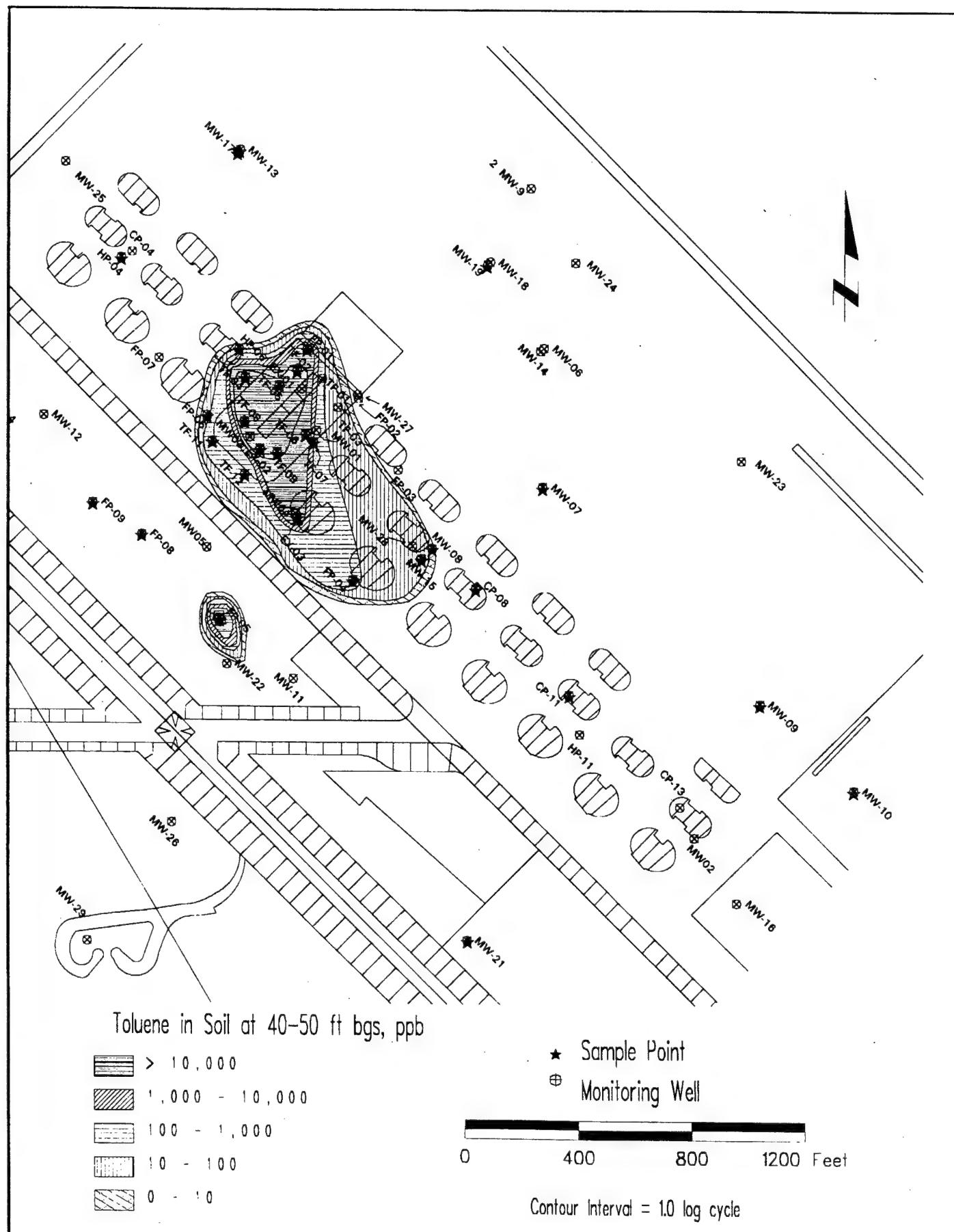
Figure A-9. Toluene contamination in soil at 40 to 50 ft deep at the Panero site.

Figure A-10. Ethylbenzene in soil at OU 3 at 20–30 ft bgs.

Figure A-11. Ethylbenzene in soil at OU 3 at 30–40 ft bgs.
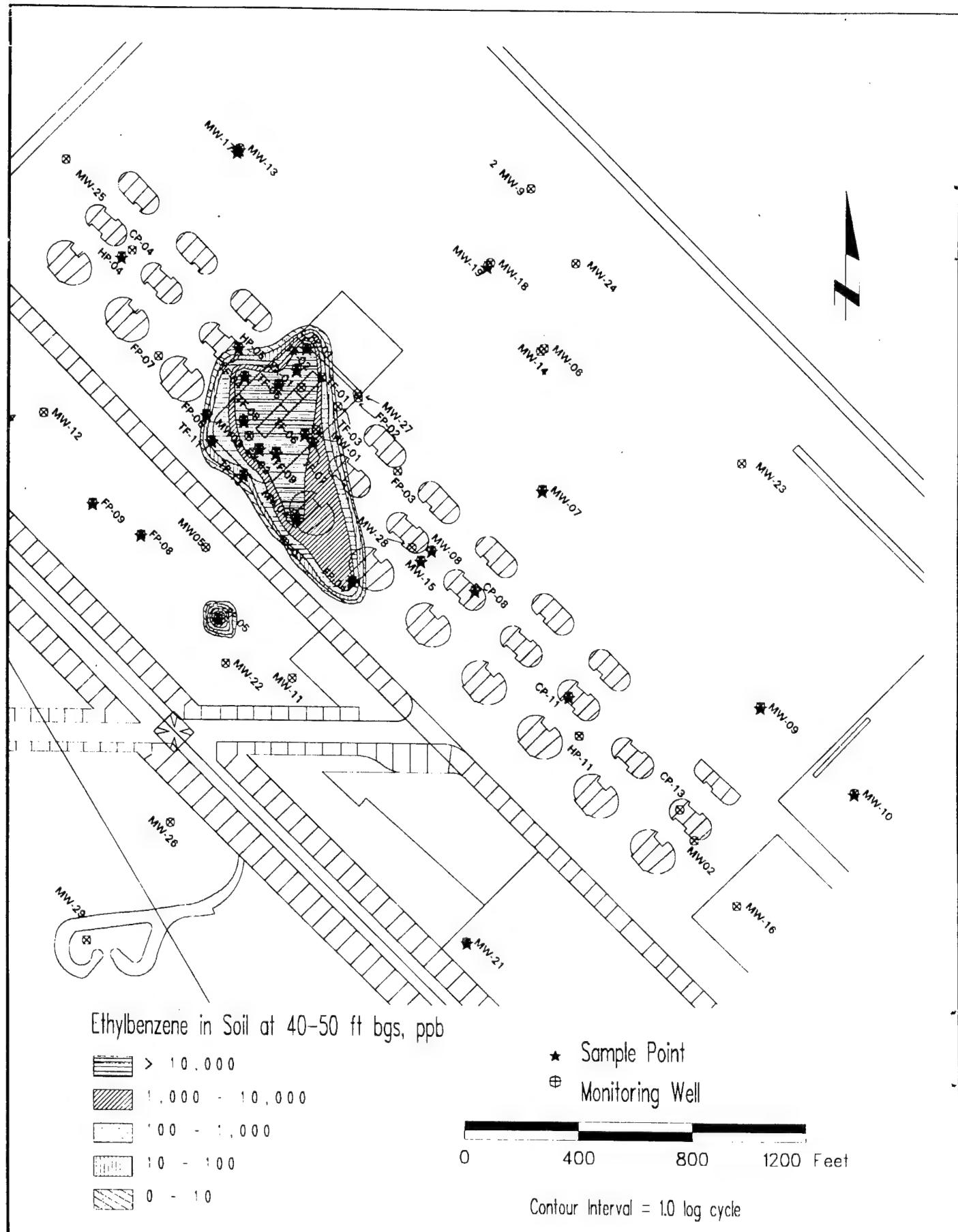
Figure A-12. Ethylbenzene contamination in soil at 40 to 50 ft deep at the Panero site.

A-14
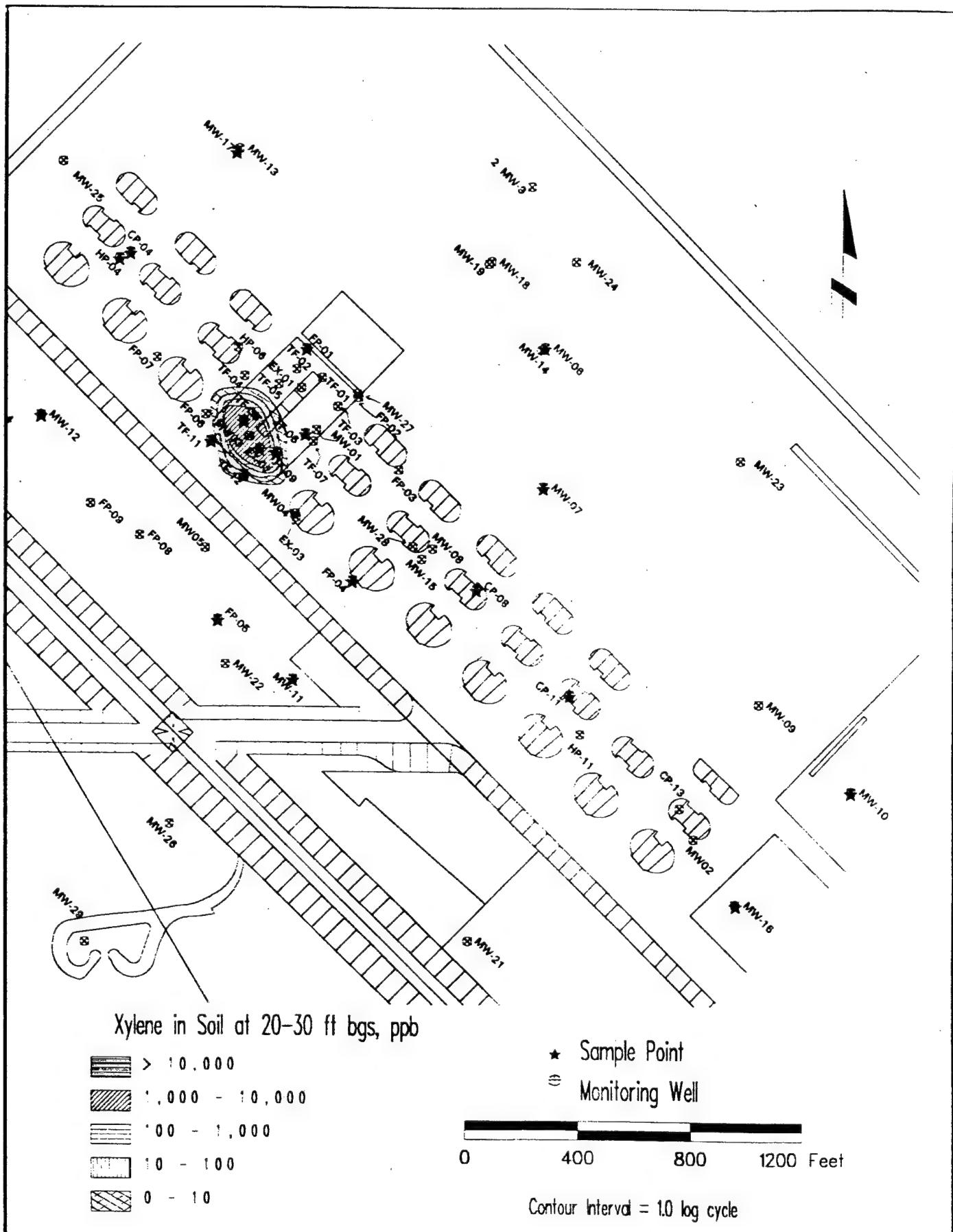
Figure A-13. Xylene contamination in soil at 20 to 30 ft deep at the Panero site.
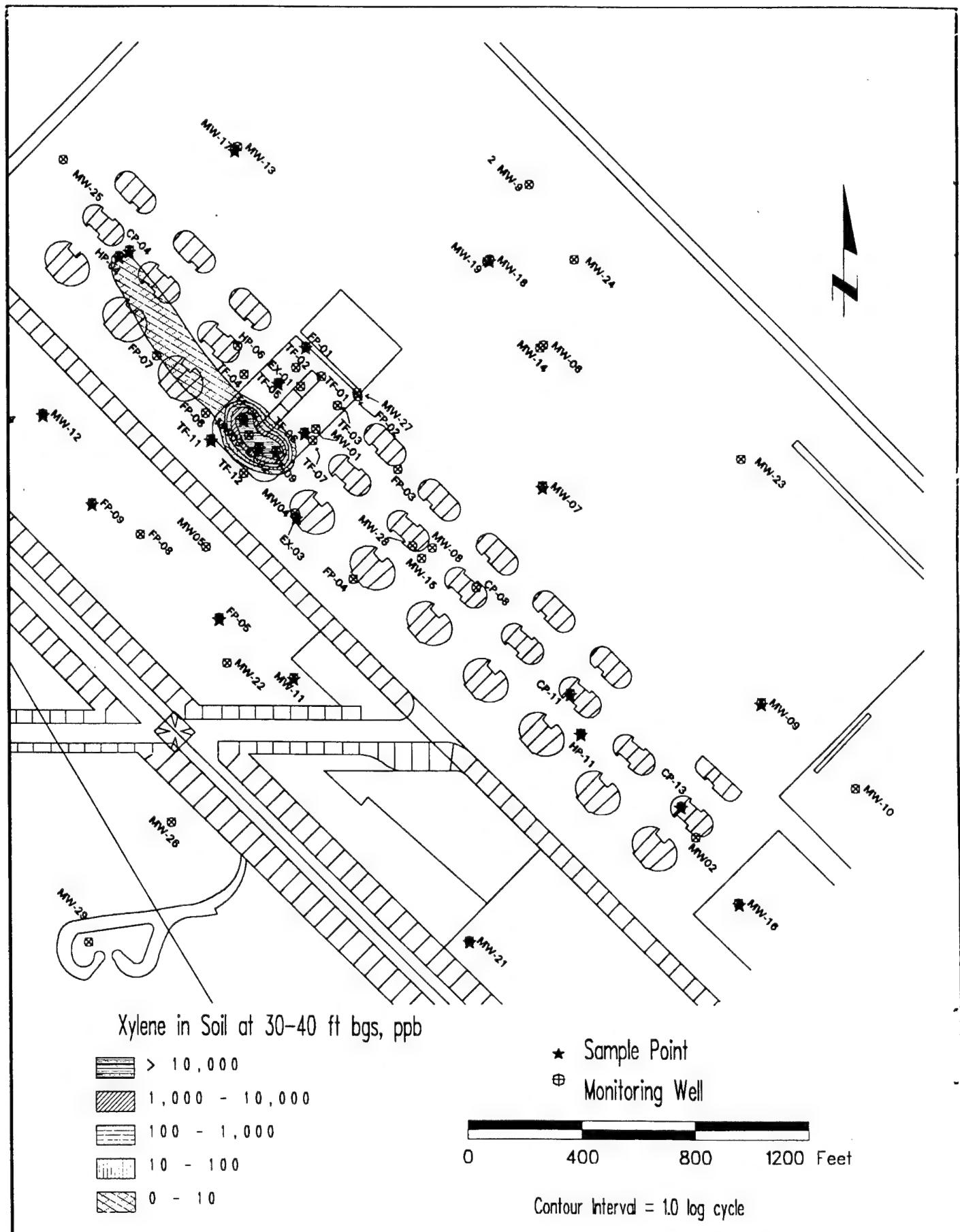
Figure A-14. Xylene contamination in soil at 30 to 40 ft deep at the Panero site.
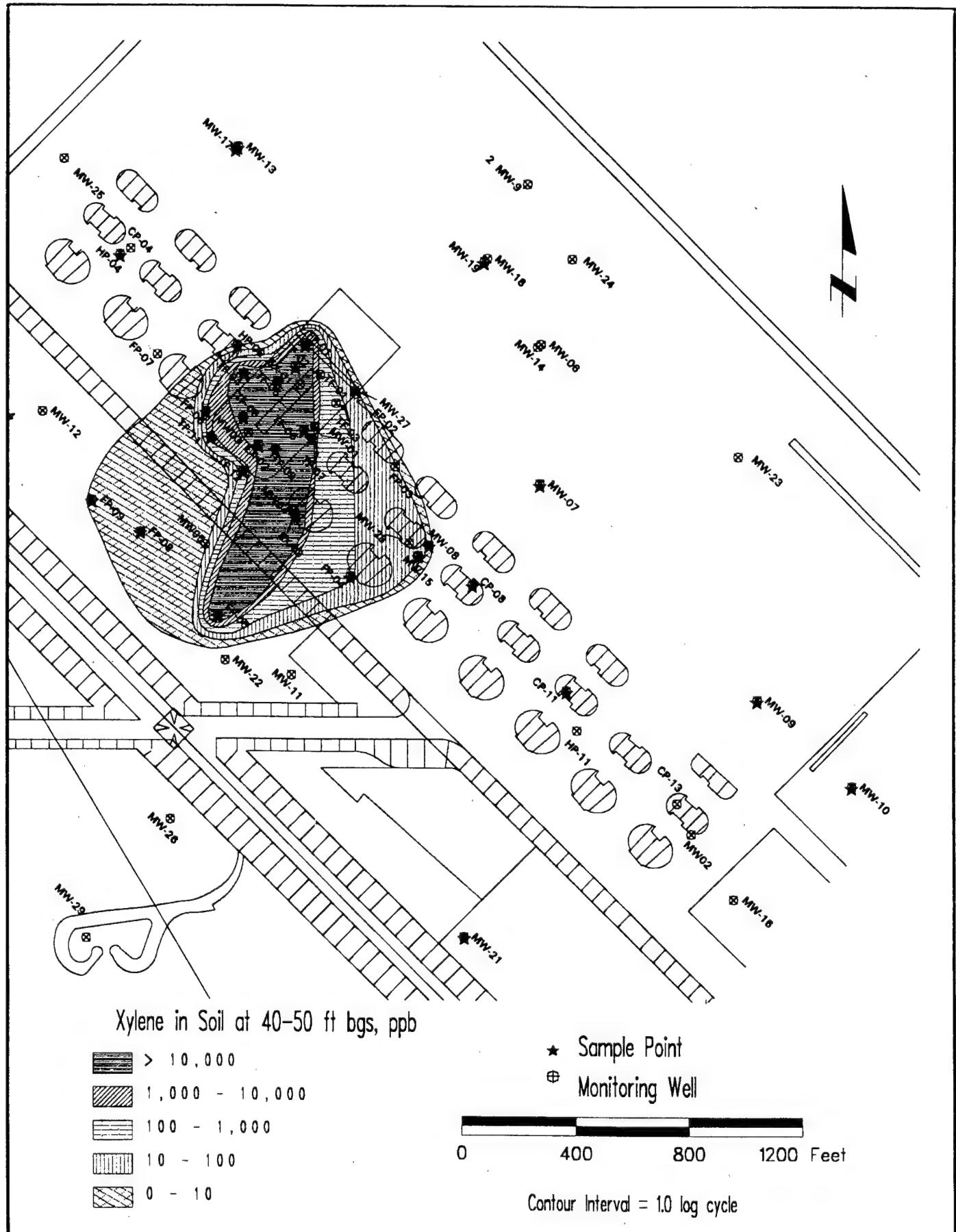
Figure A-15. Xylene contamination in soil at 40 to 50 ft deep at the Panero site.
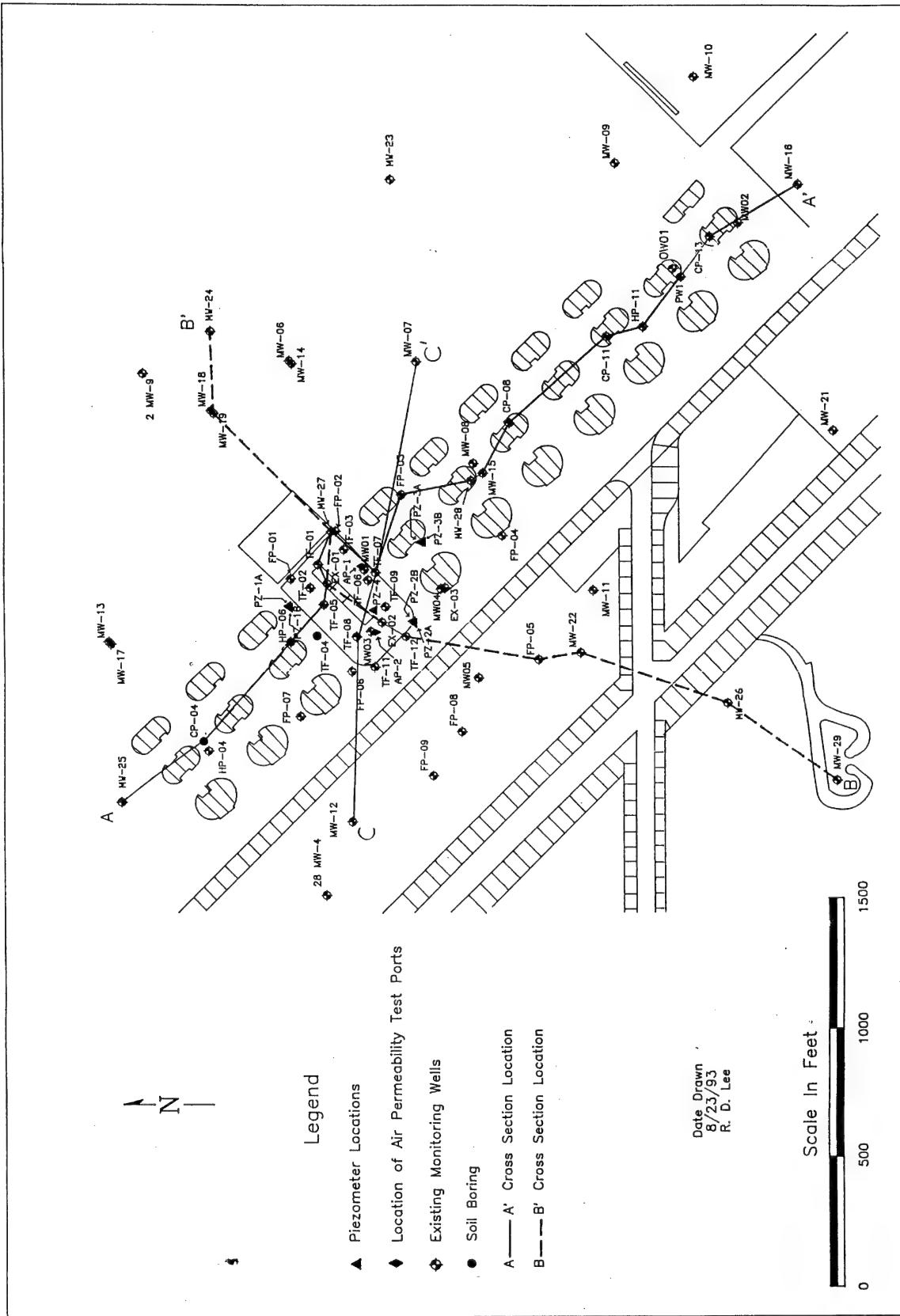
Figure A-16. Groundwater monitoring well and transect locations at OU 3.
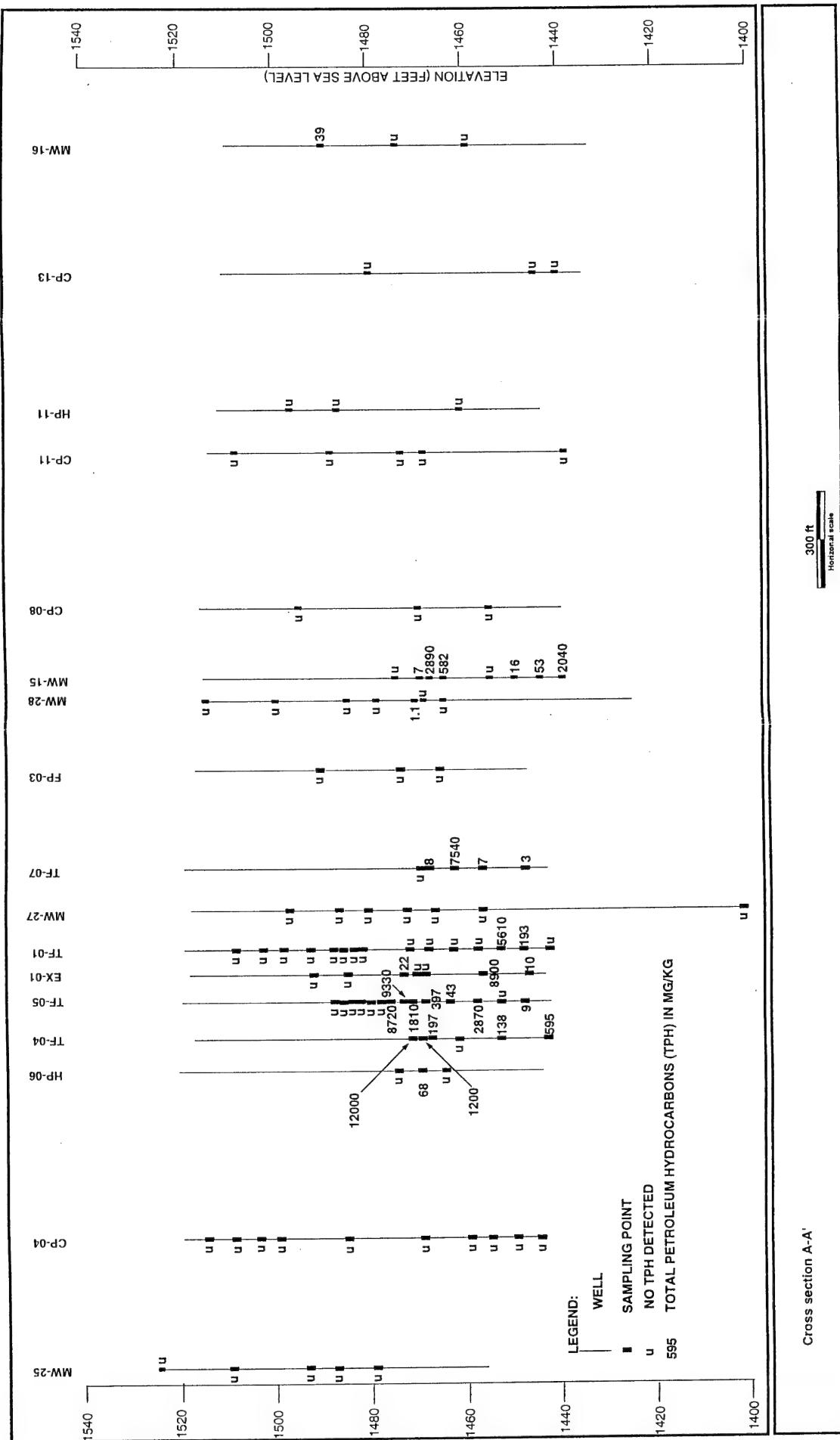
Figure A-17. Cross section of total petroleum hydrocarbon contamination in soil at the Panero site.
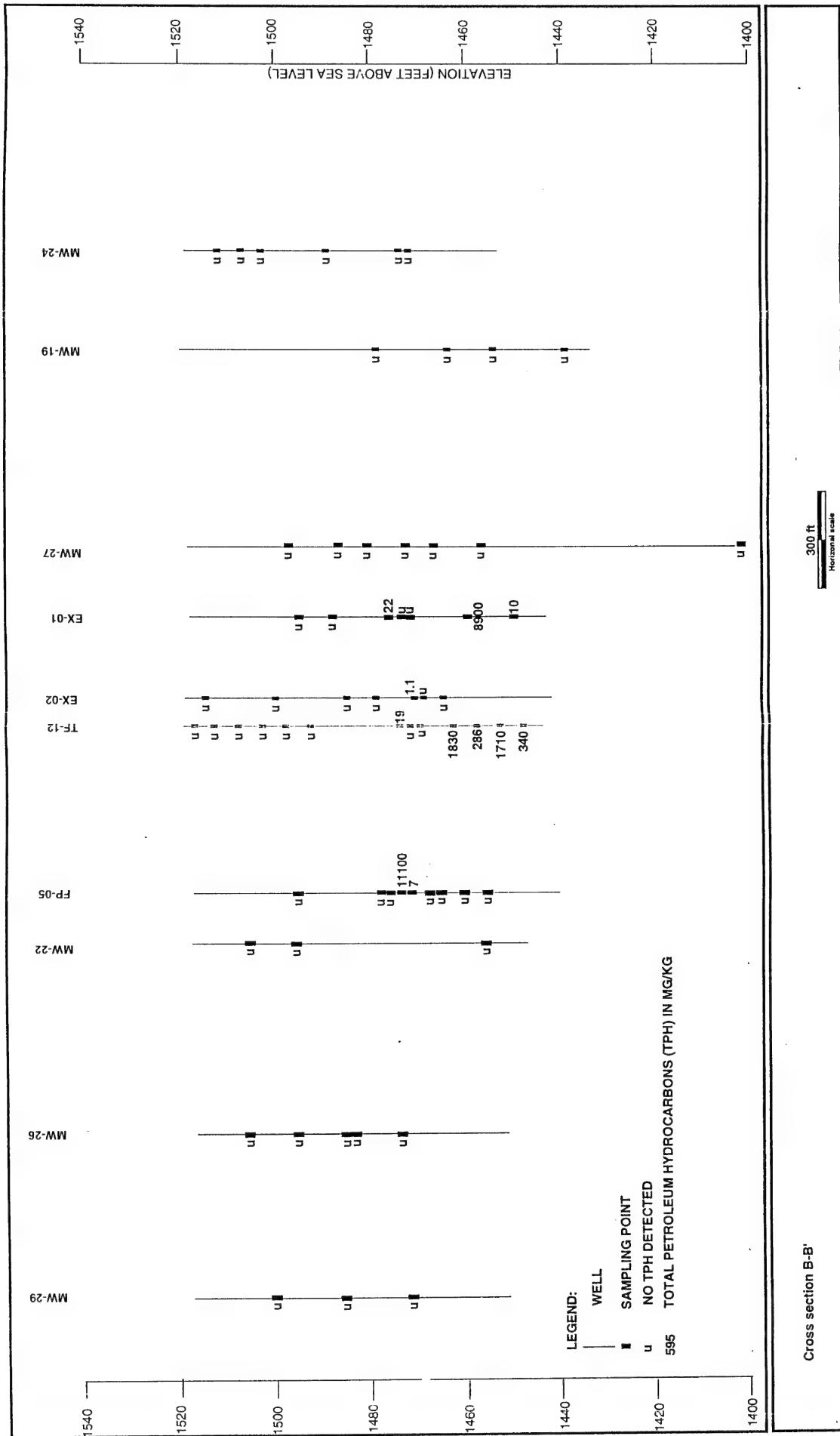
Figure A-18. Cross section of total petroleum hydrocarbon contamination in soil at the Panero site.

A-23

Apparent JP-4 Thickness, March 1993

Scale (ft)

0.00   200.00   400.00   600.00   800.00
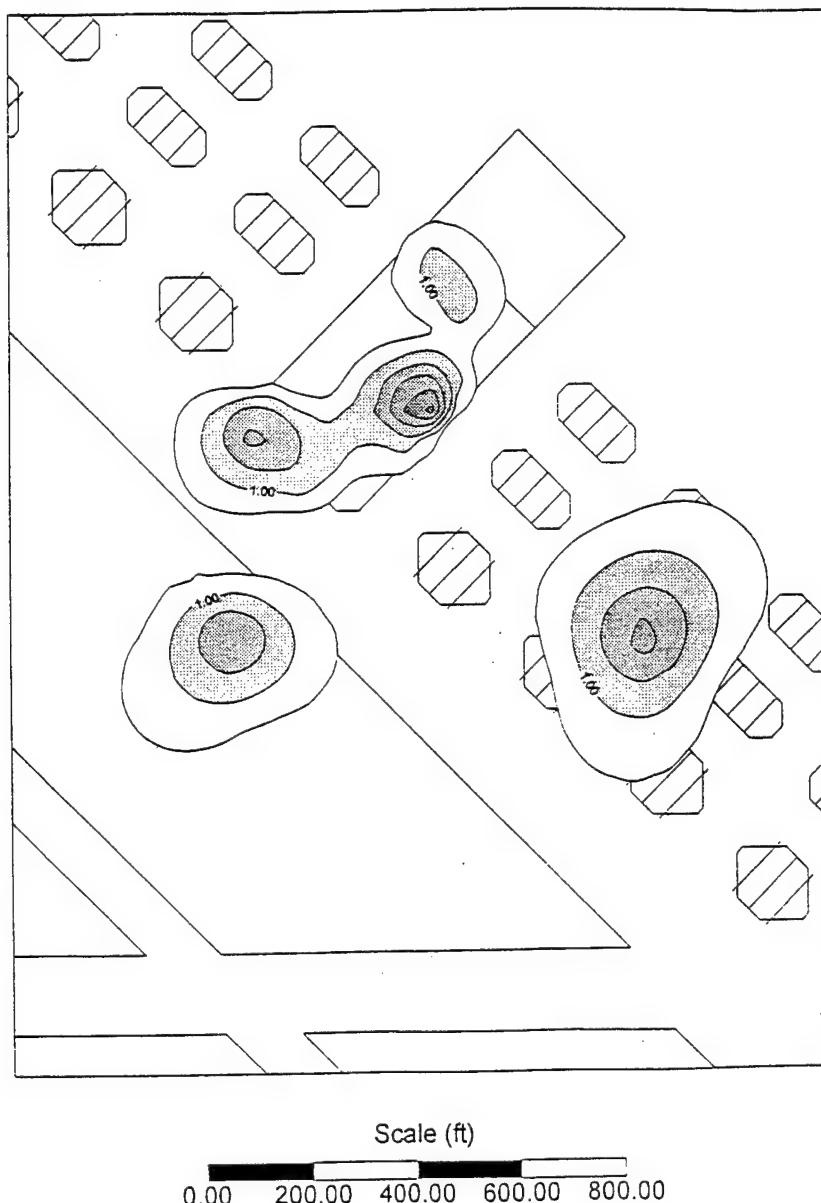
Figure A-19. Apparent JP-4 thickness, March 1993.

Apparent JP-4 Thickness, June 1993

Scale (ft)

0.00   200.00   400.00   600.00   800.00
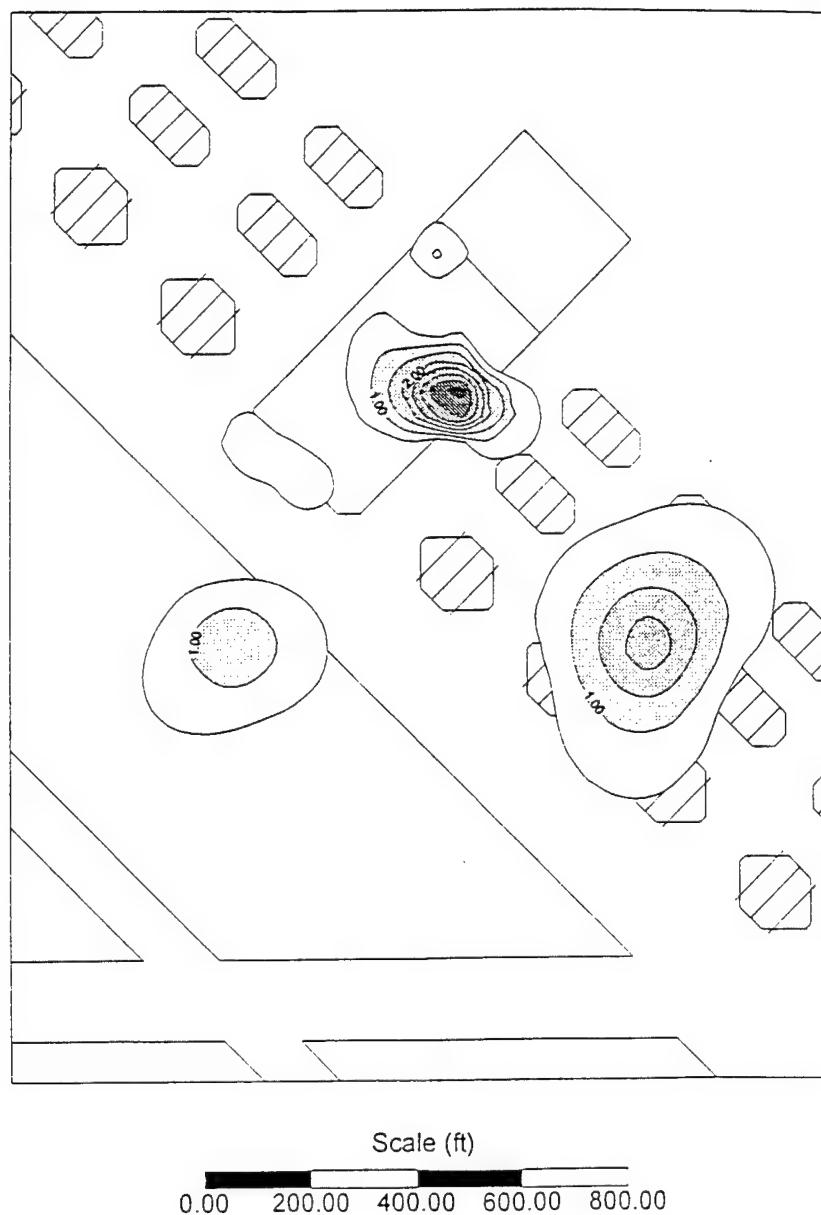
Figure A-20. Apparent JP-4 thickness, June 1993.

Apparent JP-4 Thickness, September 1993

Scale (ft)

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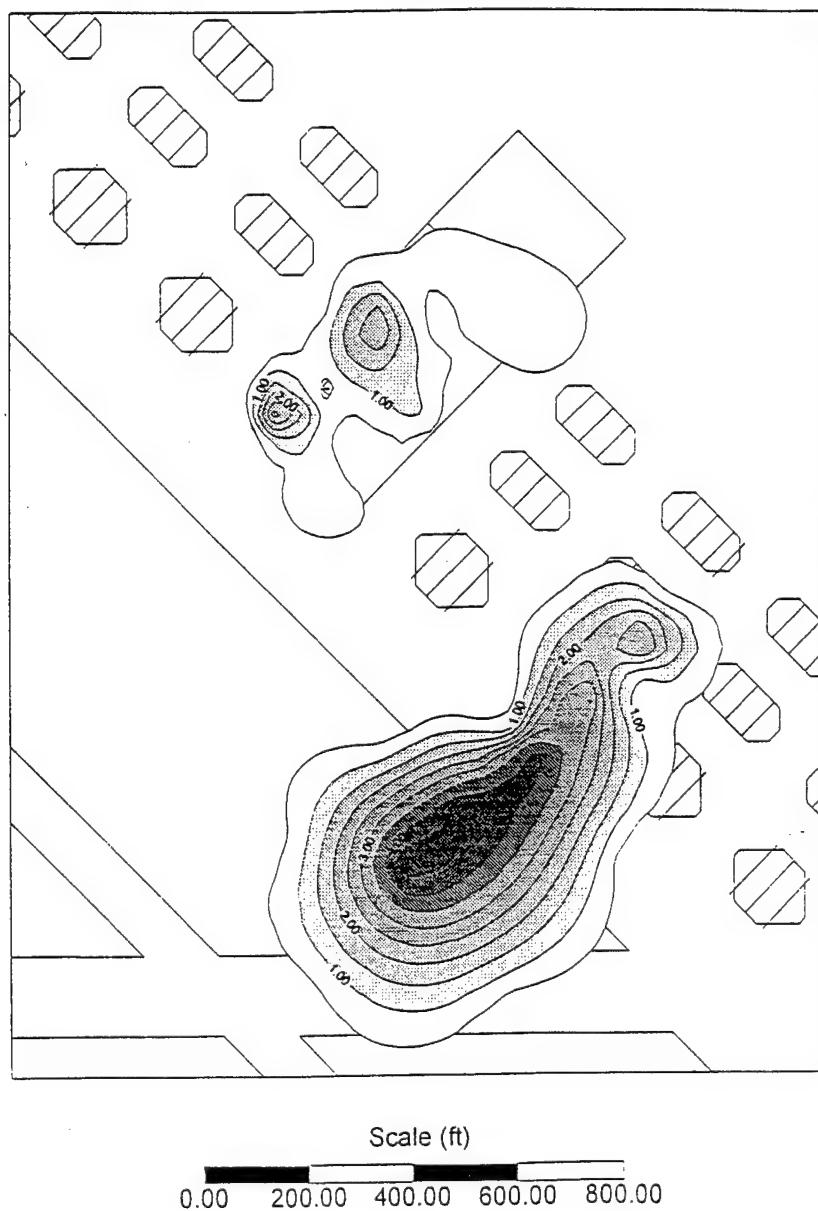
Figure A-21. Apparent JP-4 thickness, September 1993.

Apparent JP-4 Thickness, December 1993

Scale (ft)

0.00   200.00   400.00   600.00   800.00
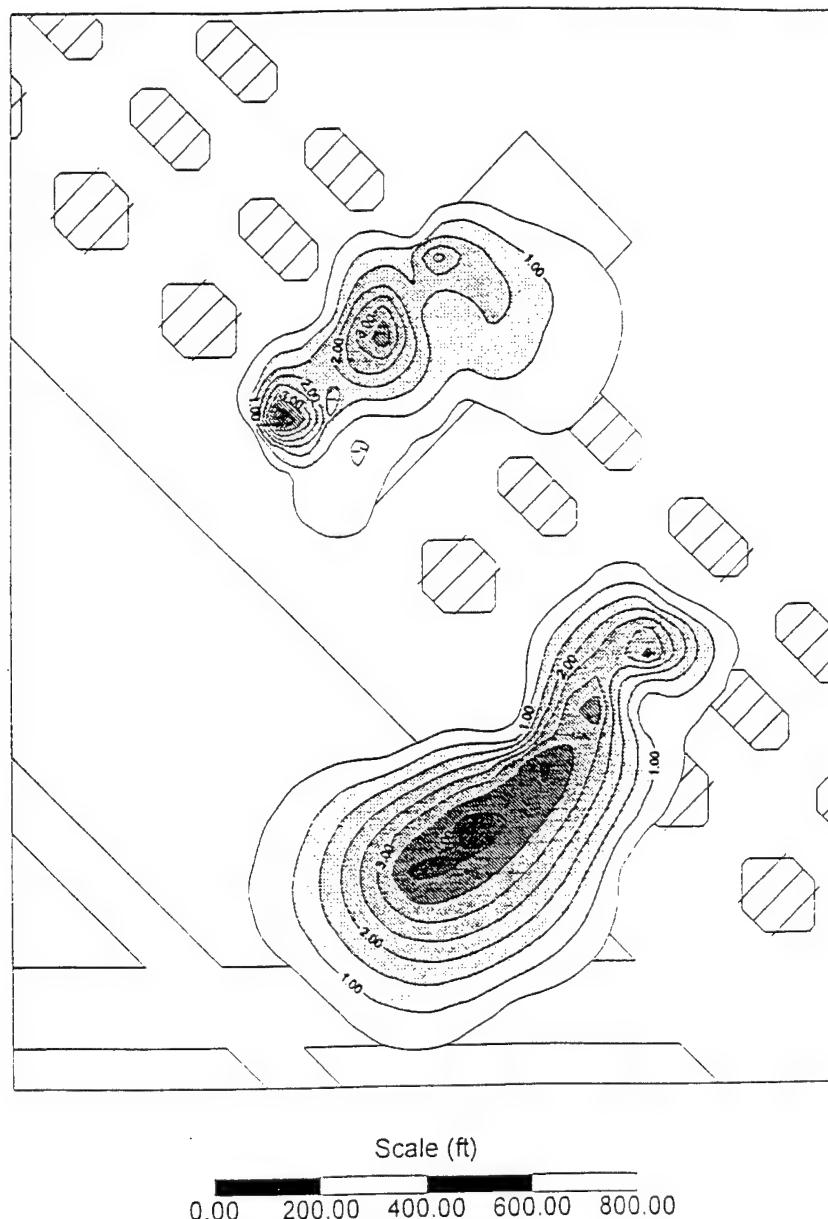
Figure A-22. Apparent JP-4 thickness, December 1993.

Apparent JP-4 Thickness, March 1994

Scale (ft)

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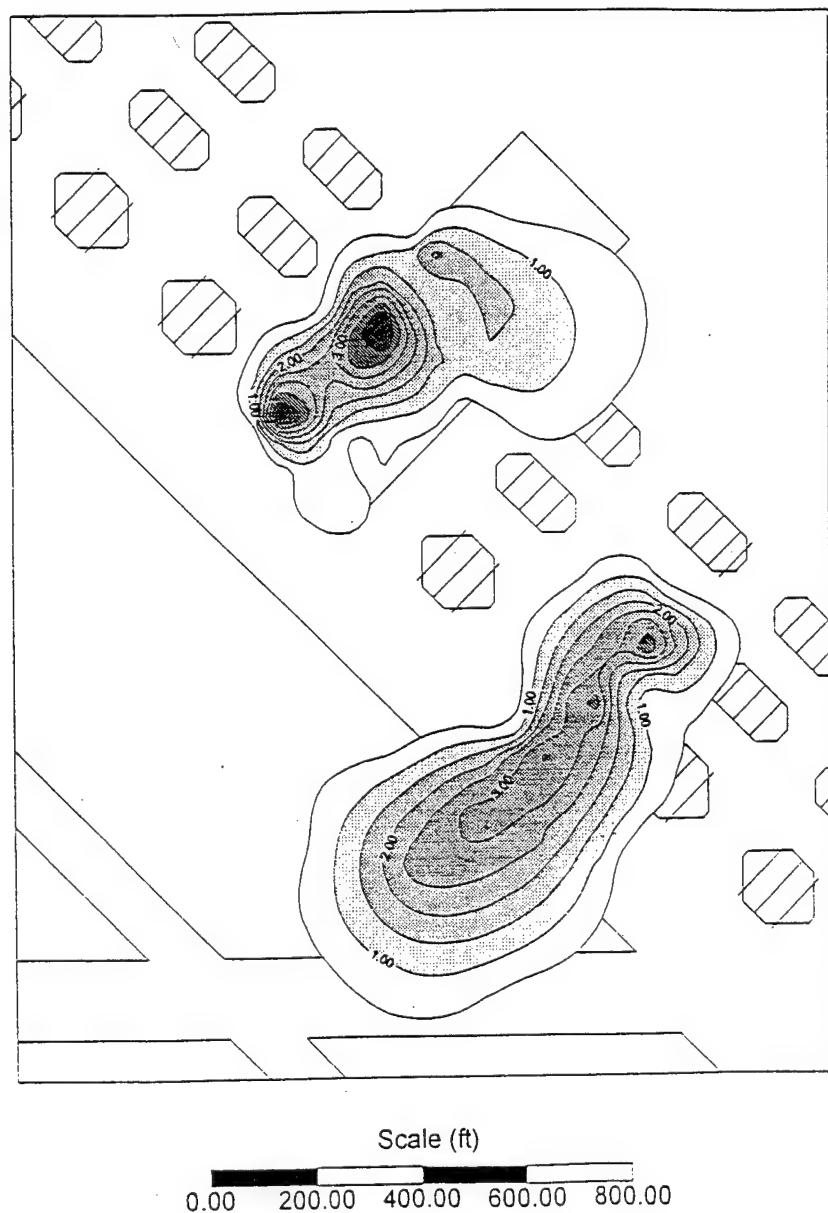
Figure A-23. Apparent JP-4 thickness, March 1994.

Apparent JP-4 Thickness, June 1994
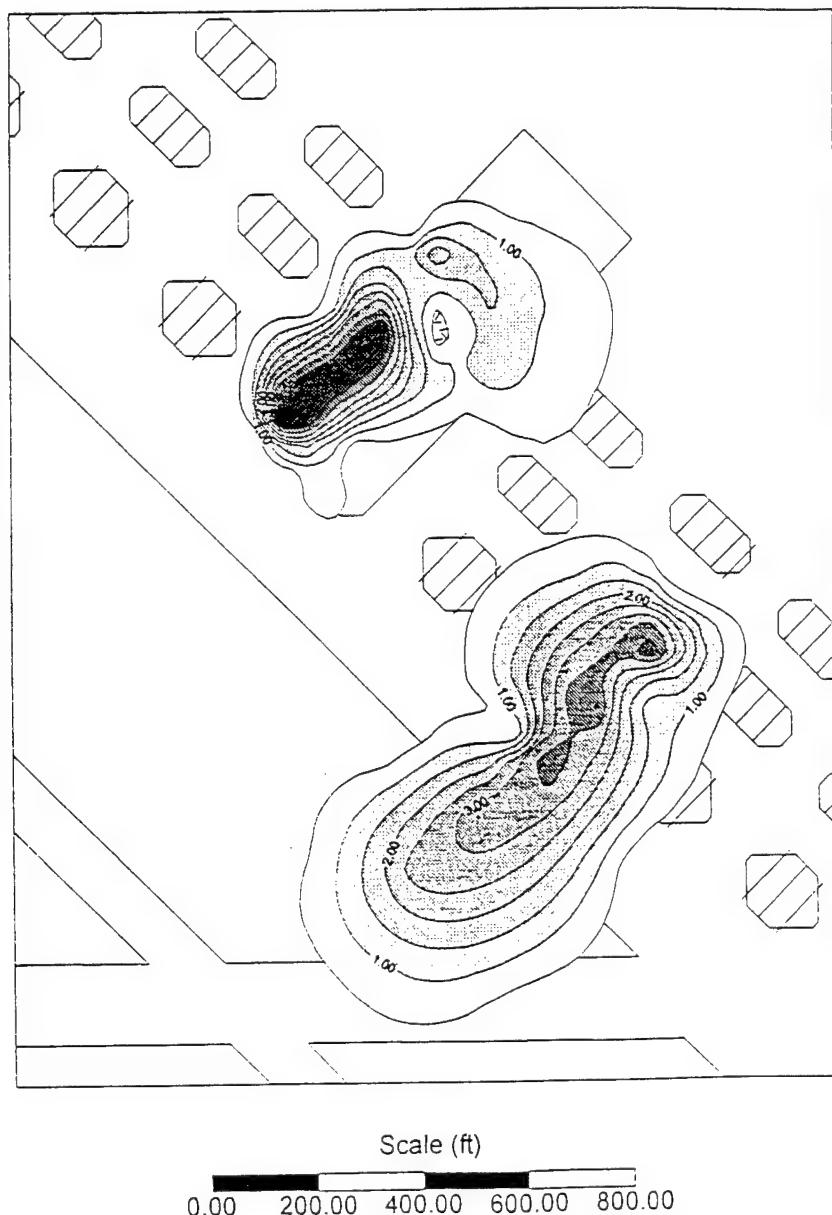
Figure A-24. Apparent JP-4 thickness, June 1994.

Apparent JP-4 Thickness, September 1994

Scale (ft)

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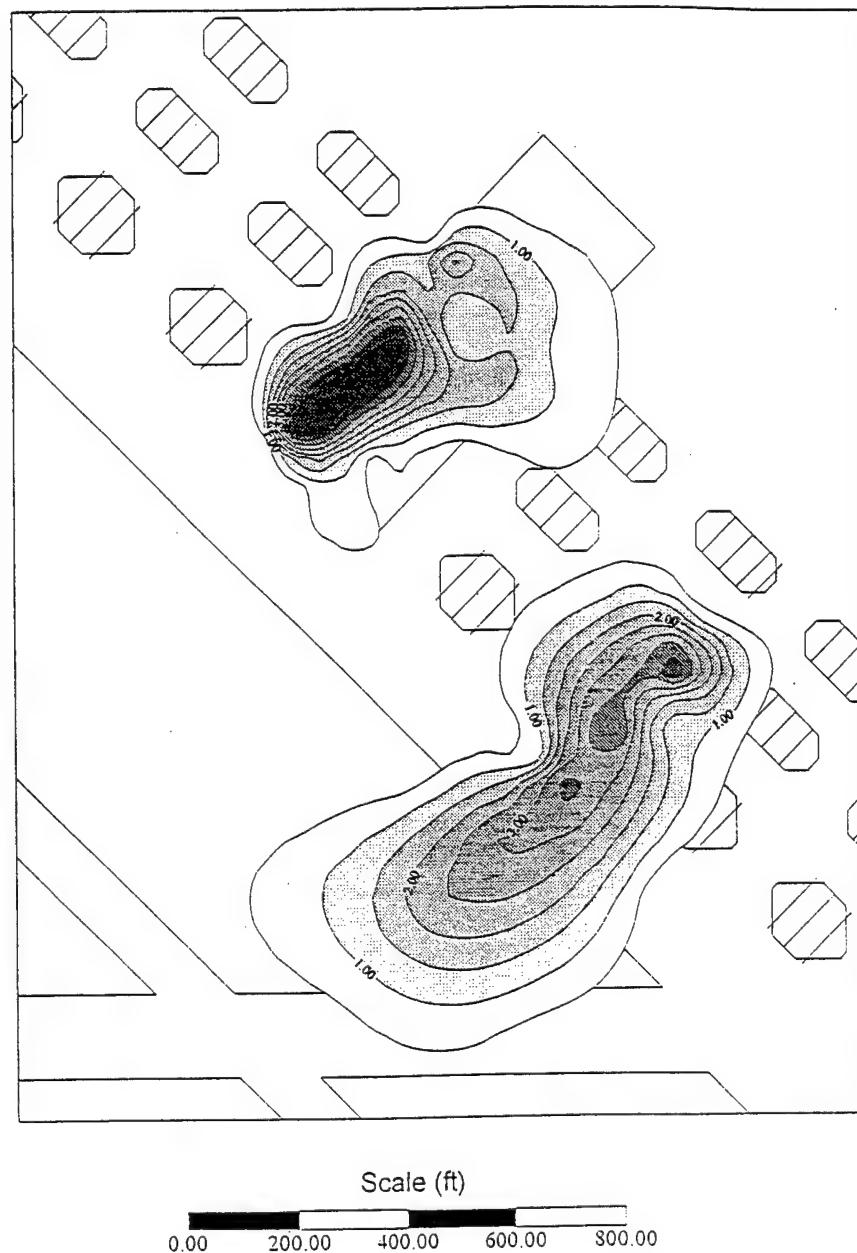
Figure A-25. Apparent JP-4 thickness, September 1994.

Apparent JP-4 Thickness, December 1994

Scale (ft)

0.00   200.00   400.00   600.00   800.00
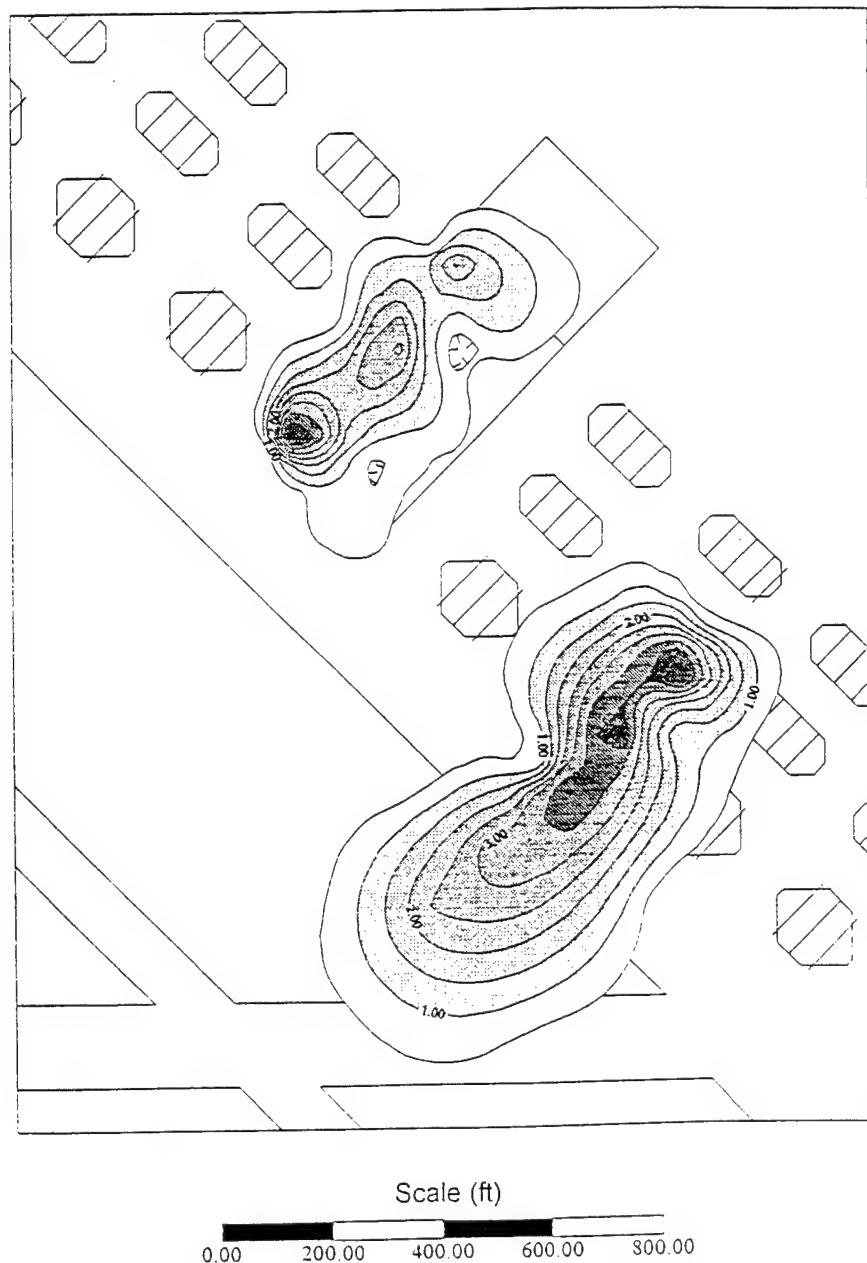
Figure A-26. Apparent JP-4 thickness, December 1994.

Apparent JP-4 Thickness, March 1995

Scale (ft)

0.00   200.00   400.00   600.00   800.00

Figure A-27. Apparent JP-4 thickness, March 1995.
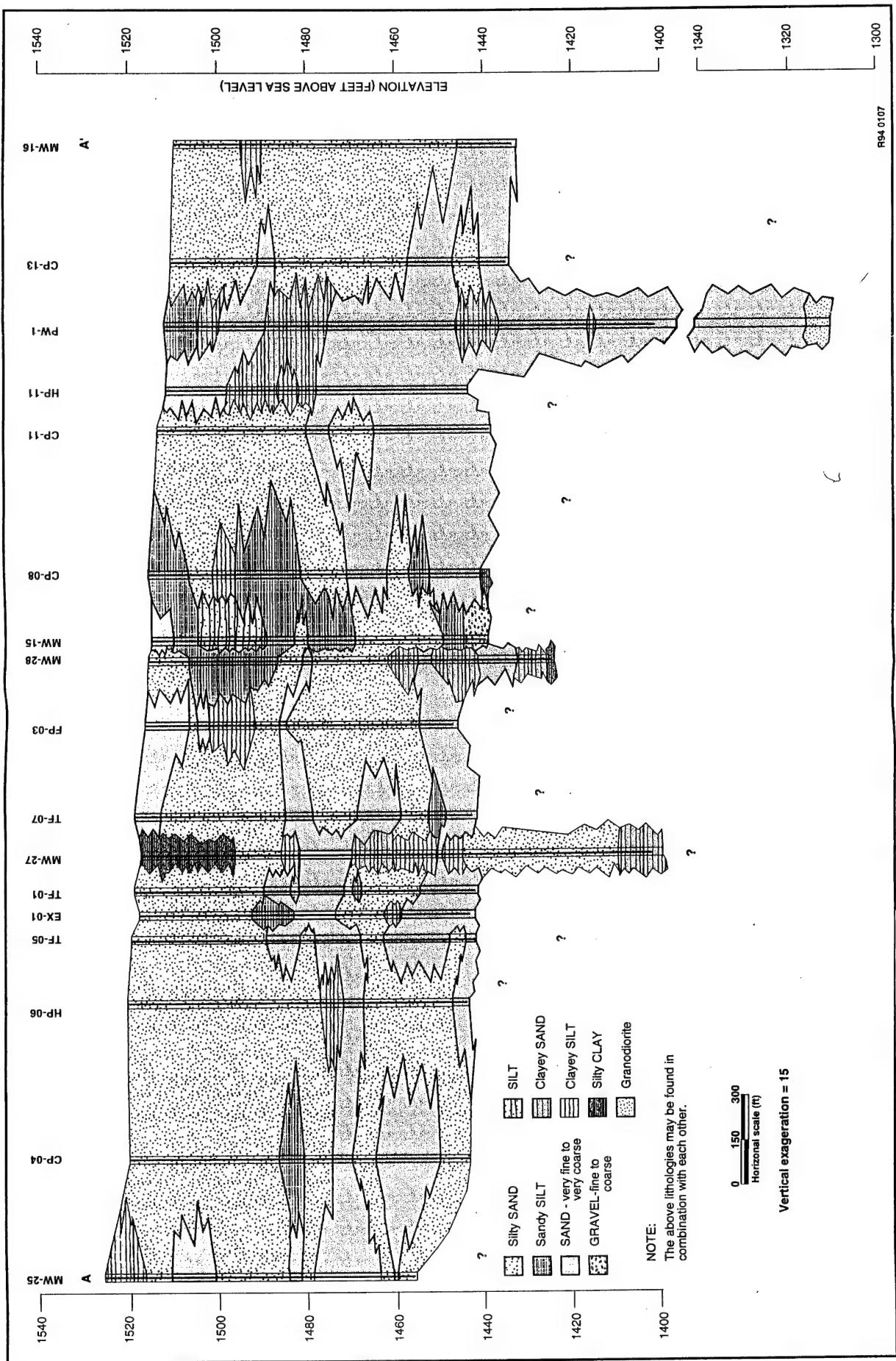
Figure A-28. Northwest-southeast lithologic cross-section A-A' through the Panero site.

A-35
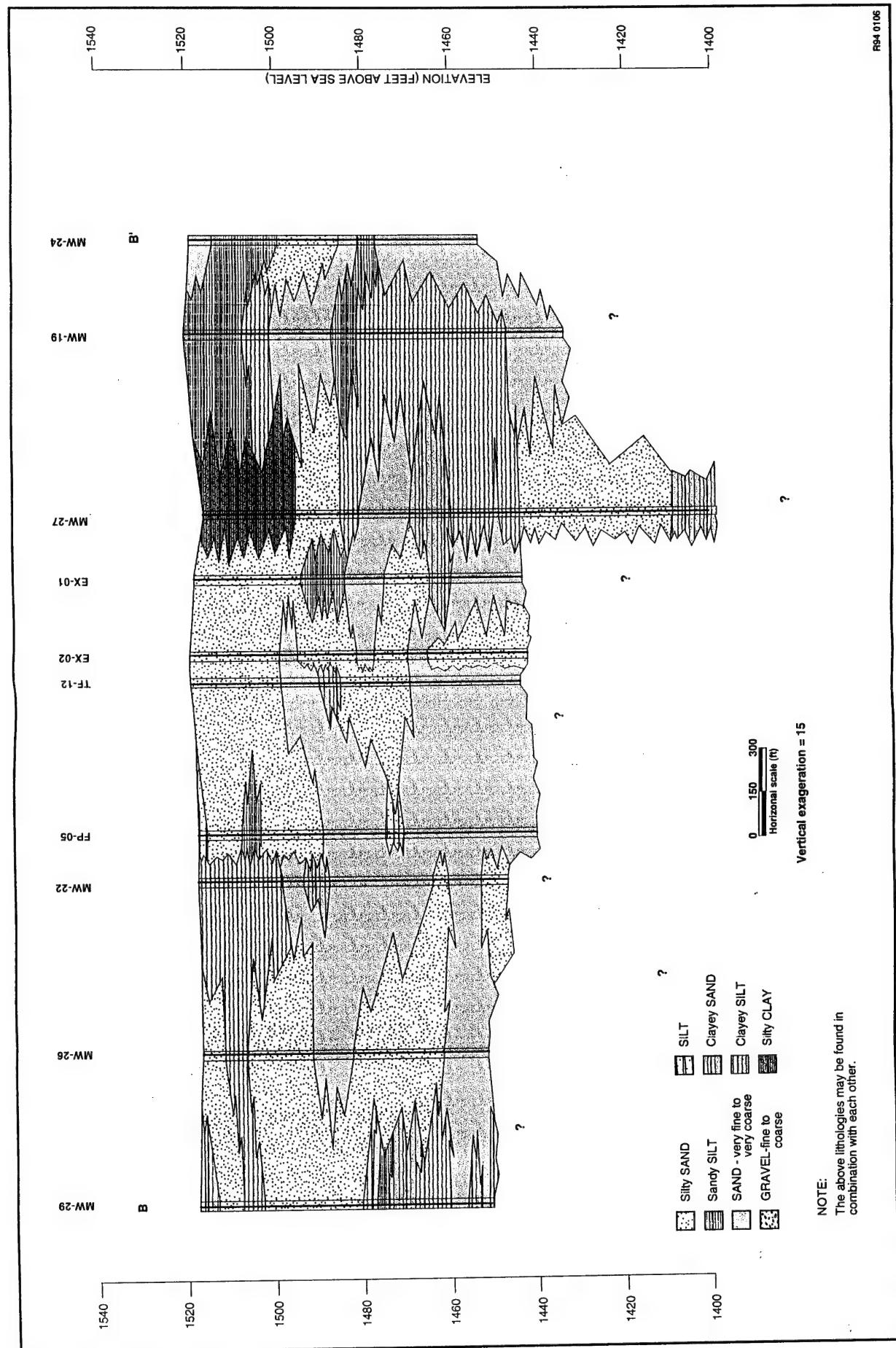
Figure A-29. Northeast-southwest lithologic cross-section B-B' through the Panero site.

A-37

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Benzene concentrations (ug/L), 3rd Quarter
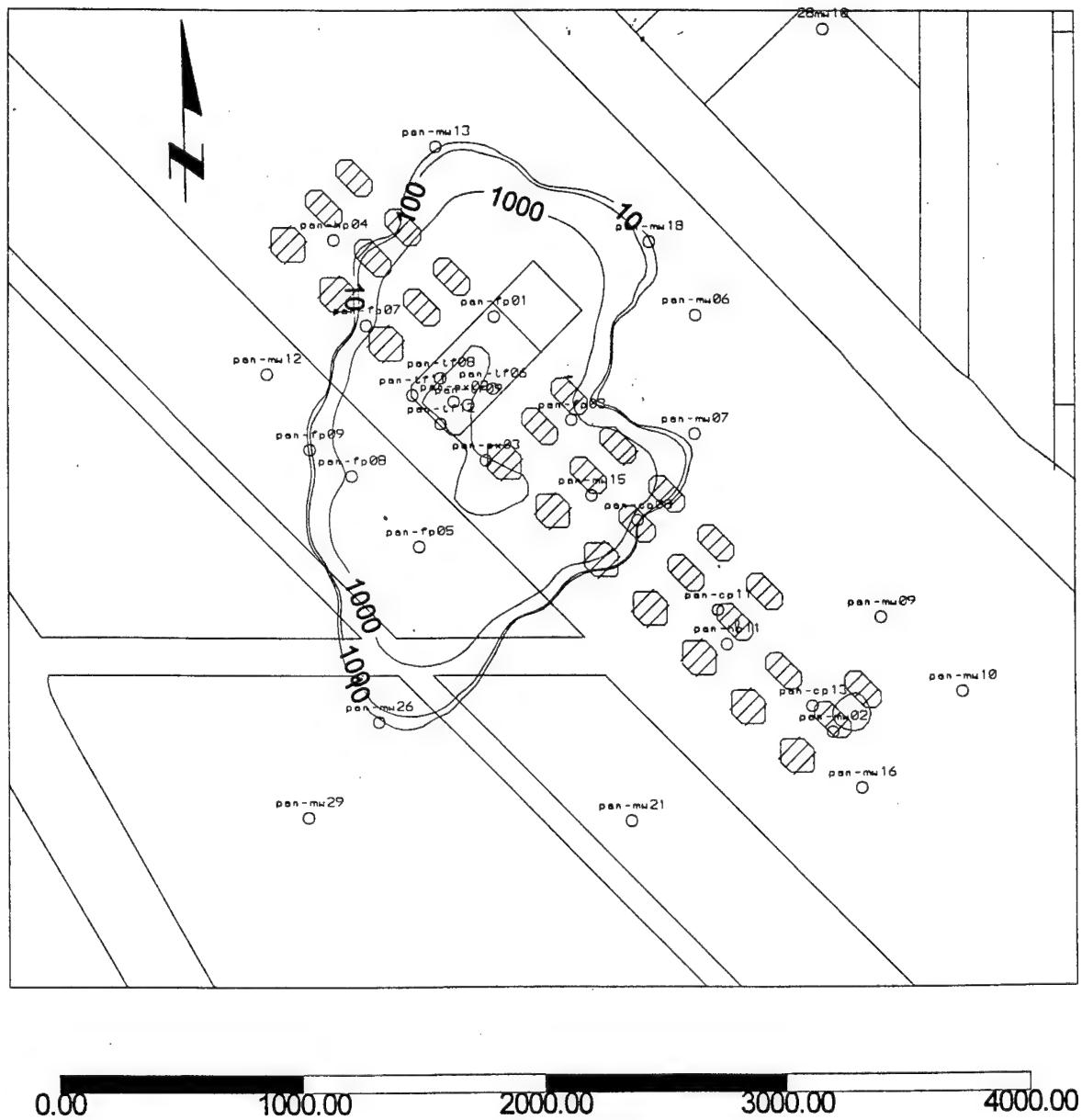
Figure A-30. Benzene concentrations in groundwater at OU 3 for Quarter 3 (approximately 12/92).

Benzene concentrations (ug/L), 4th Quarter
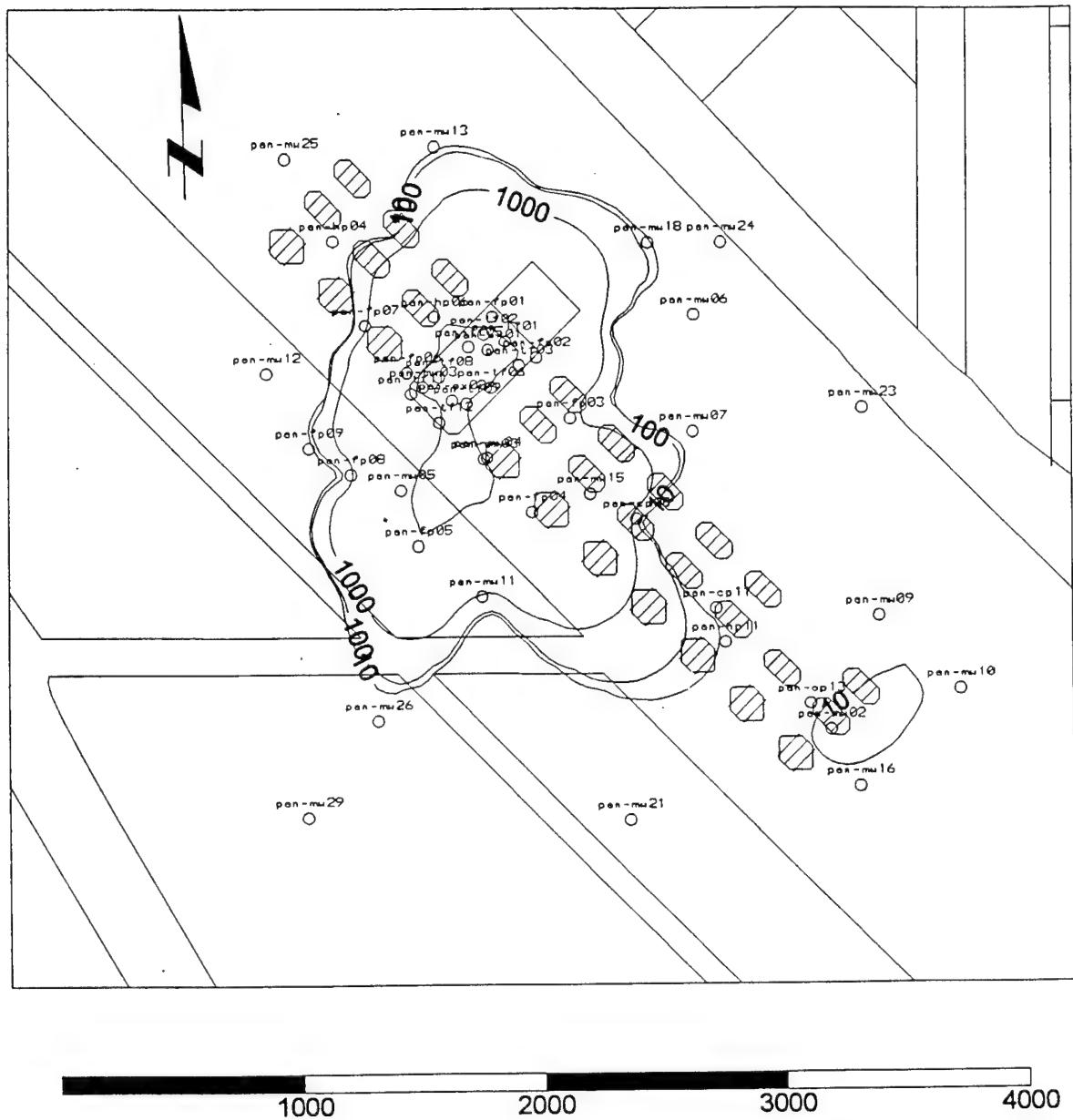
Figure A-31. Benzene concentrations in groundwater at OU 3 for Quarter 4 (approximately 3/93).

Benzene concentrations (ug/L), 5th Quarter
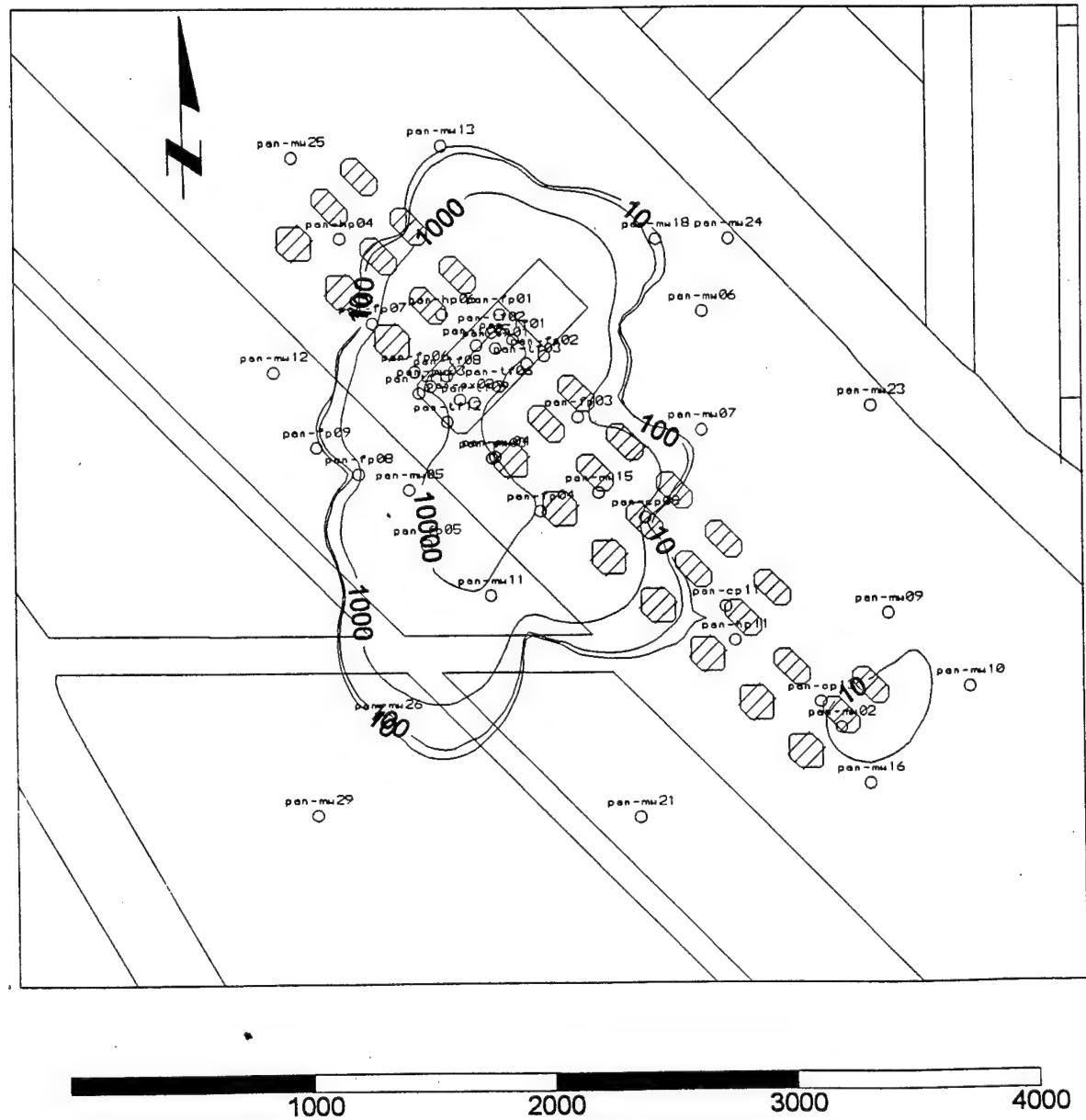
**Figure A-32.** Benzene concentrations in groundwater at OU 3 for Quarter 5 (approximately 6/93).

Benzene concentrations (ug/L), 6th Quarter
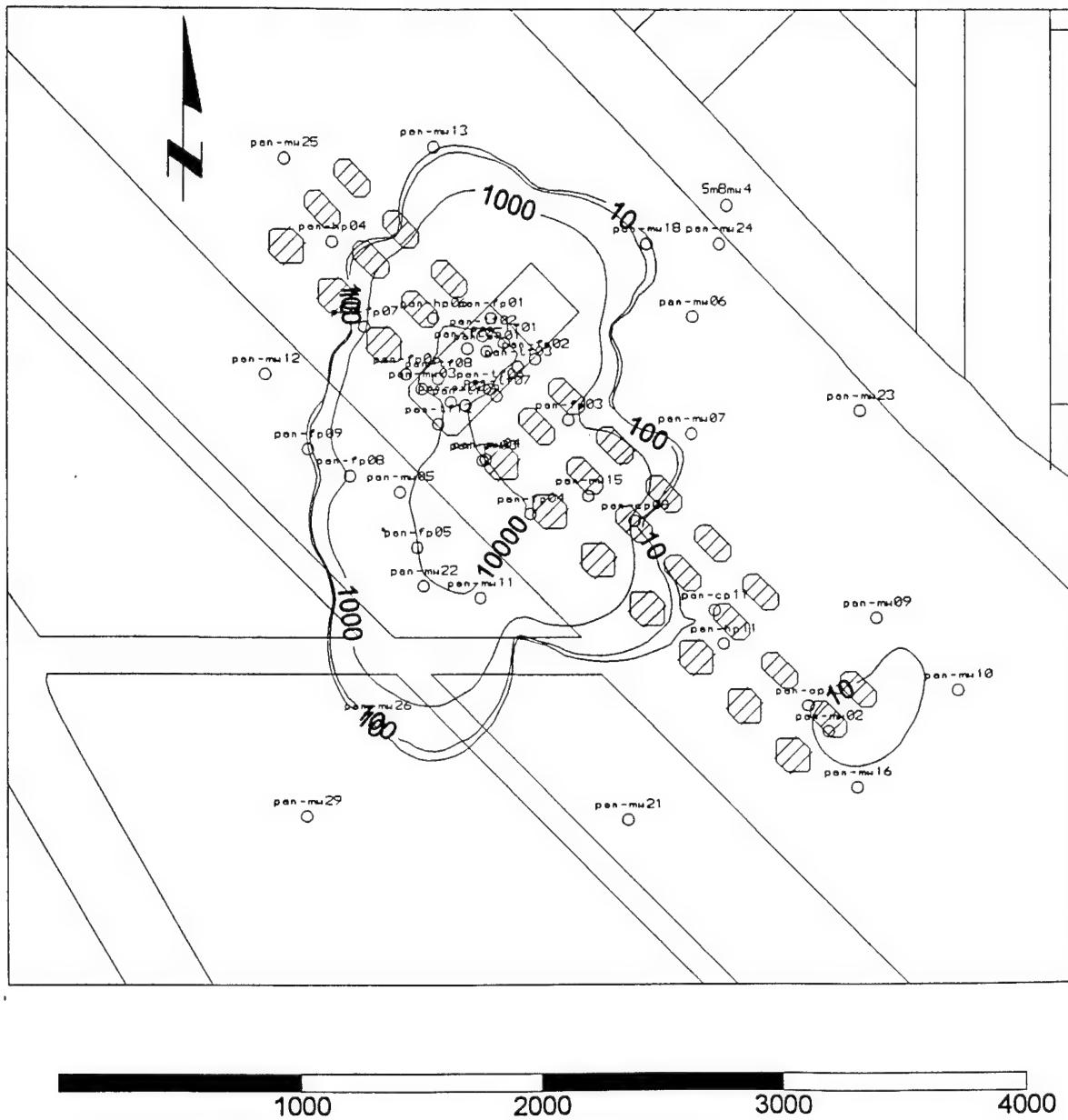
Figure A-33. Benzene concentrations in groundwater at OU 3 for Quarter 6 (approximately 9/93).

Benzene concentrations (ug/L), 7th Quarter
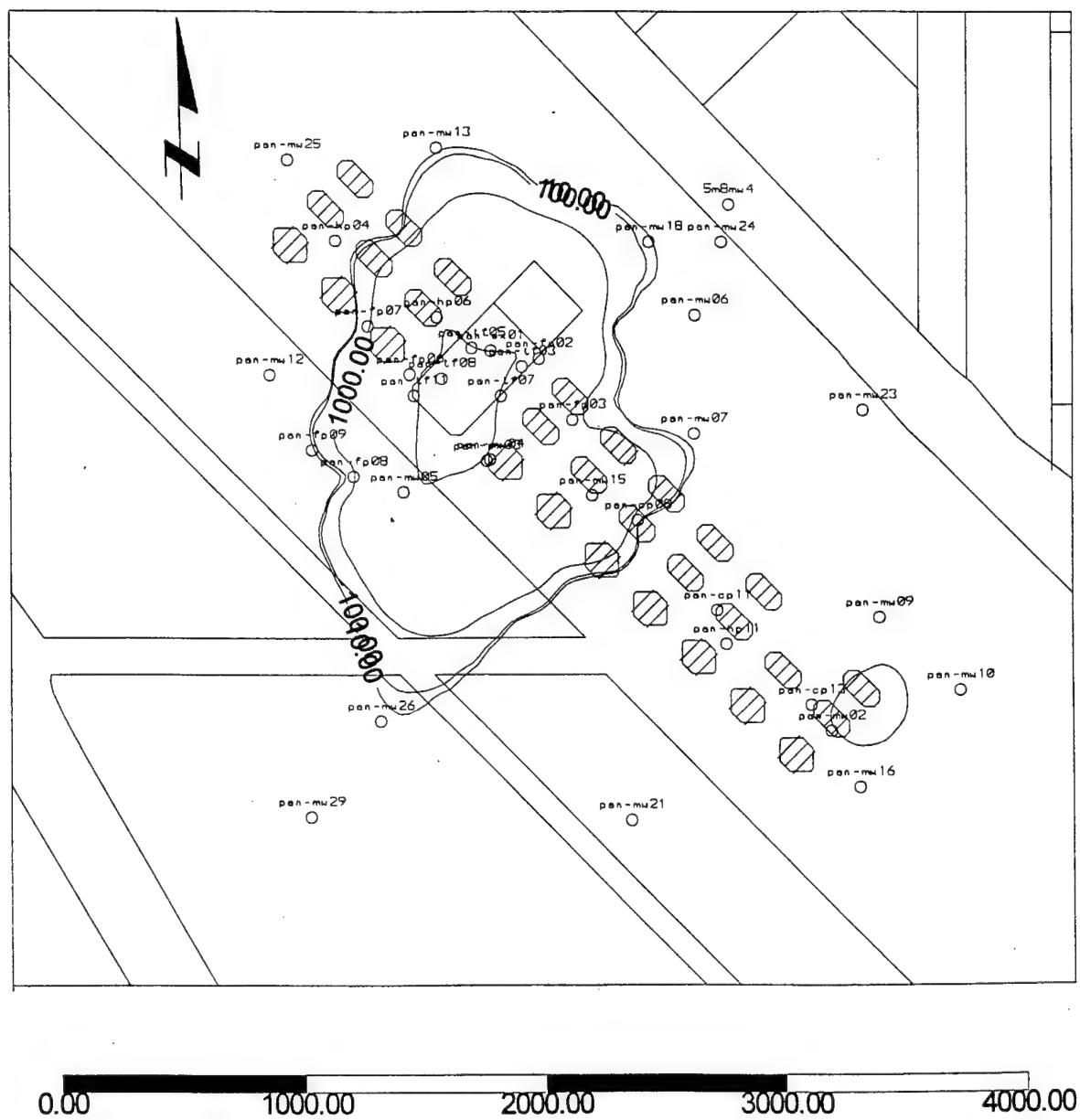
Figure A-34. Benzene concentrations in groundwater at OU 3 for Quarter 7 (approximately 12/93).

Benzene concentrations (ug/L), 8th Quarter
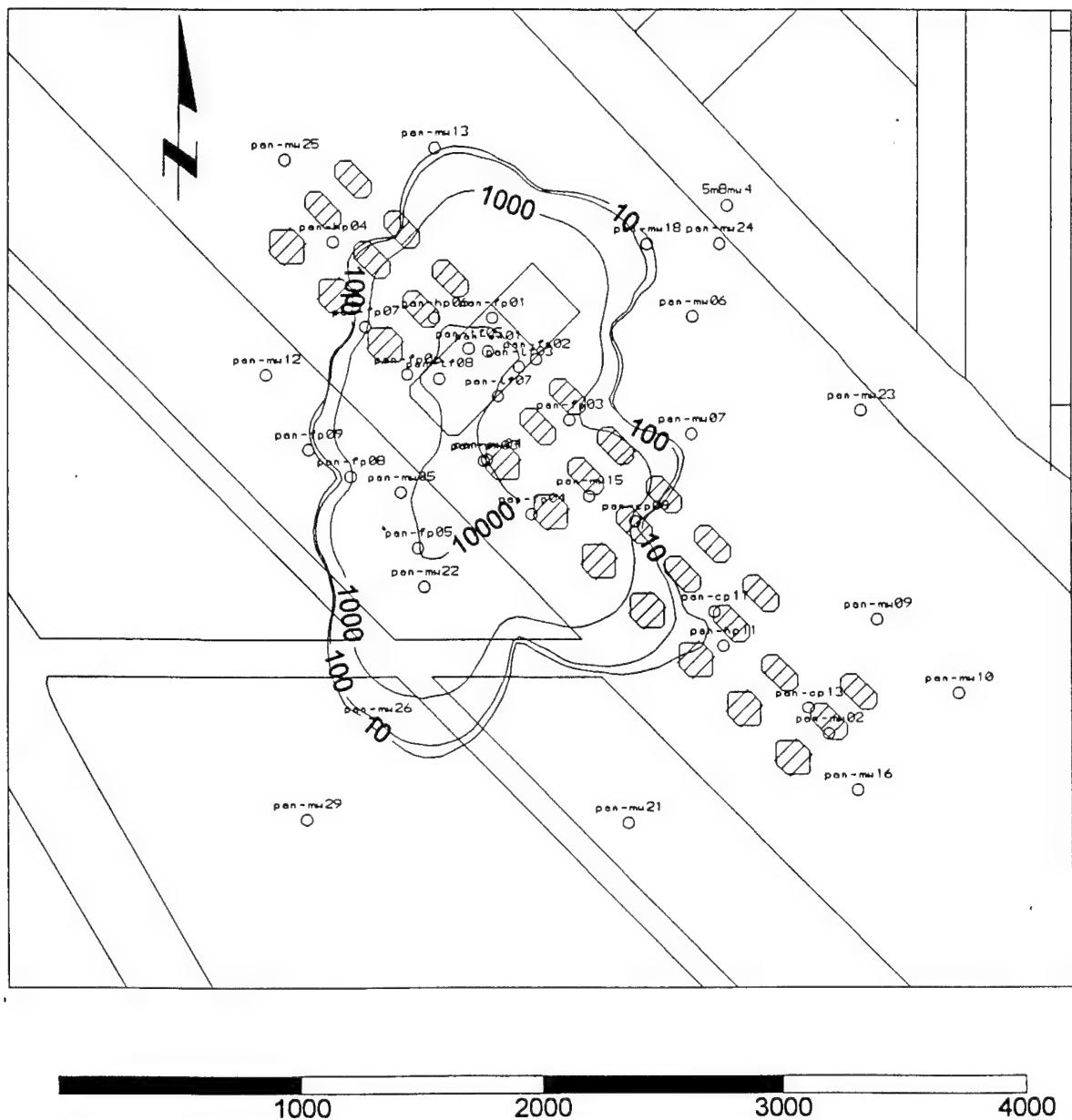
**Figure A-35.** Benzene concentrations in groundwater at OU 3 for Quarter 8 (approximately 3/94).

Benzene concentrations (ug/L) 9th Quarter
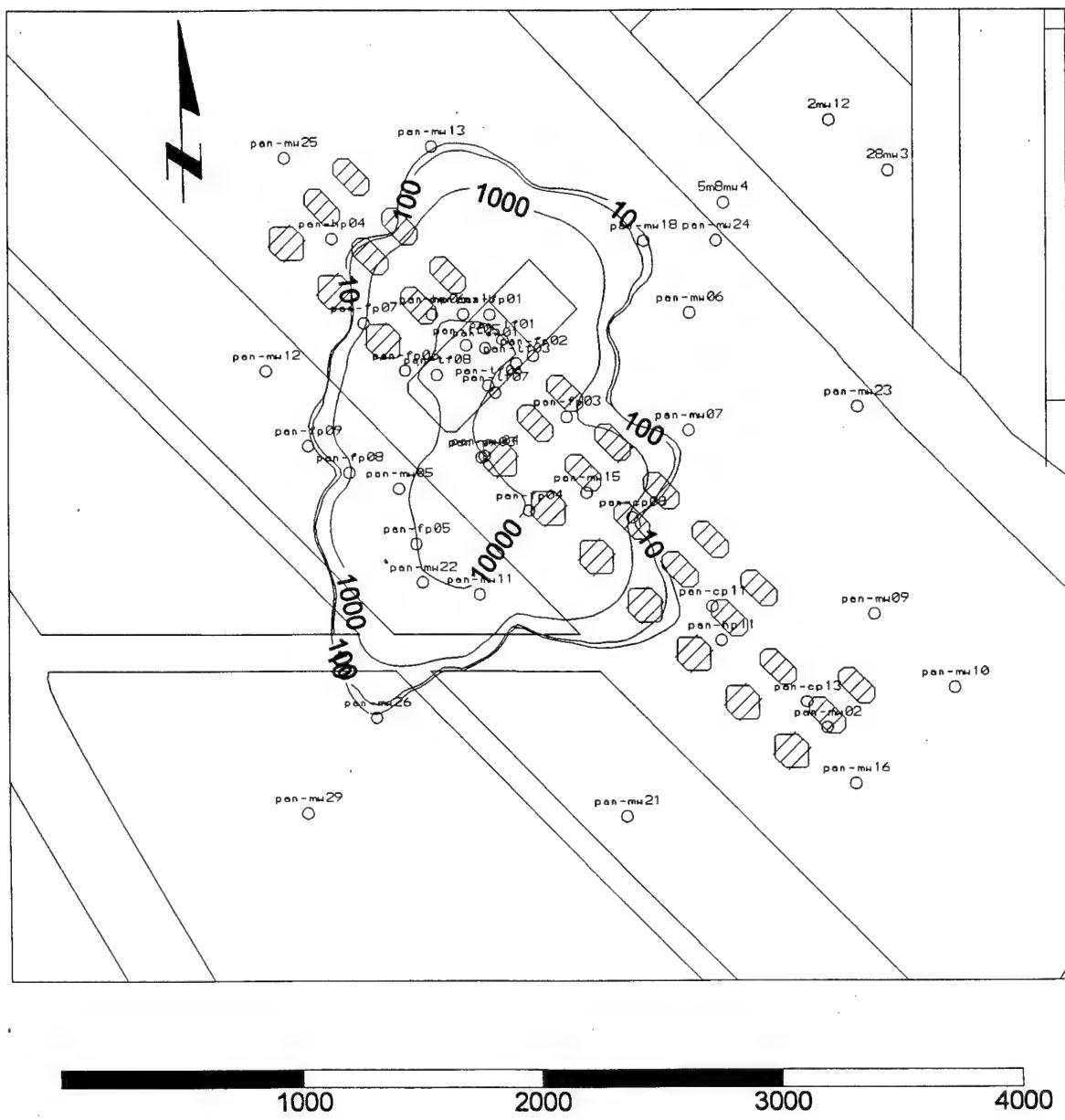


Figure A-36. Benzene concentrations in groundwater at OU 3 for Quarter 9 (approximately 6/94).

Toluene concentrations (ug/L), 3rd Quarter
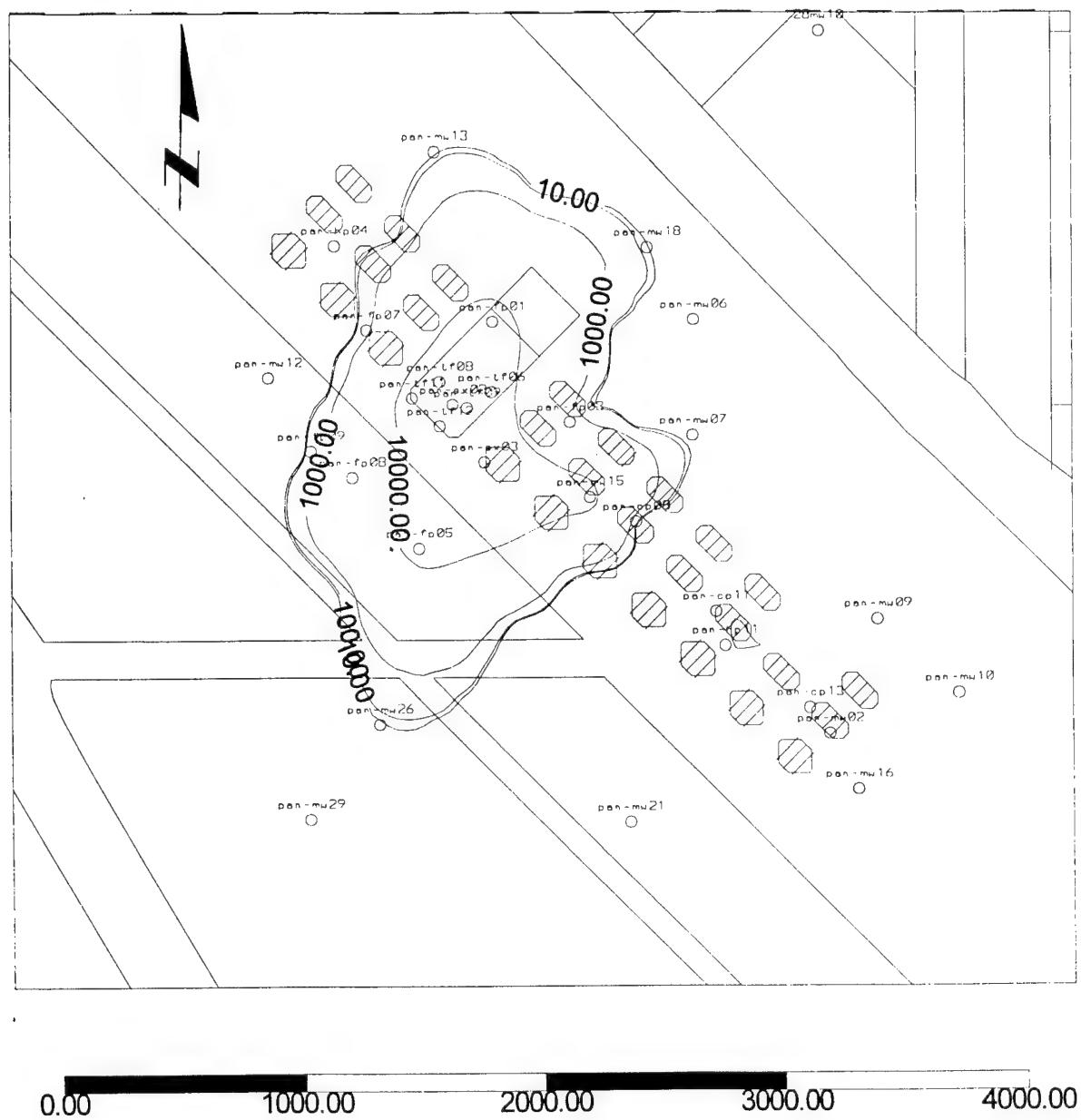
Figure A-37. Toluene concentrations in groundwater at OU 3 for Quarter 3 (approximately 12/92).

Toluene concentrations (ug/L), 4th Quarter
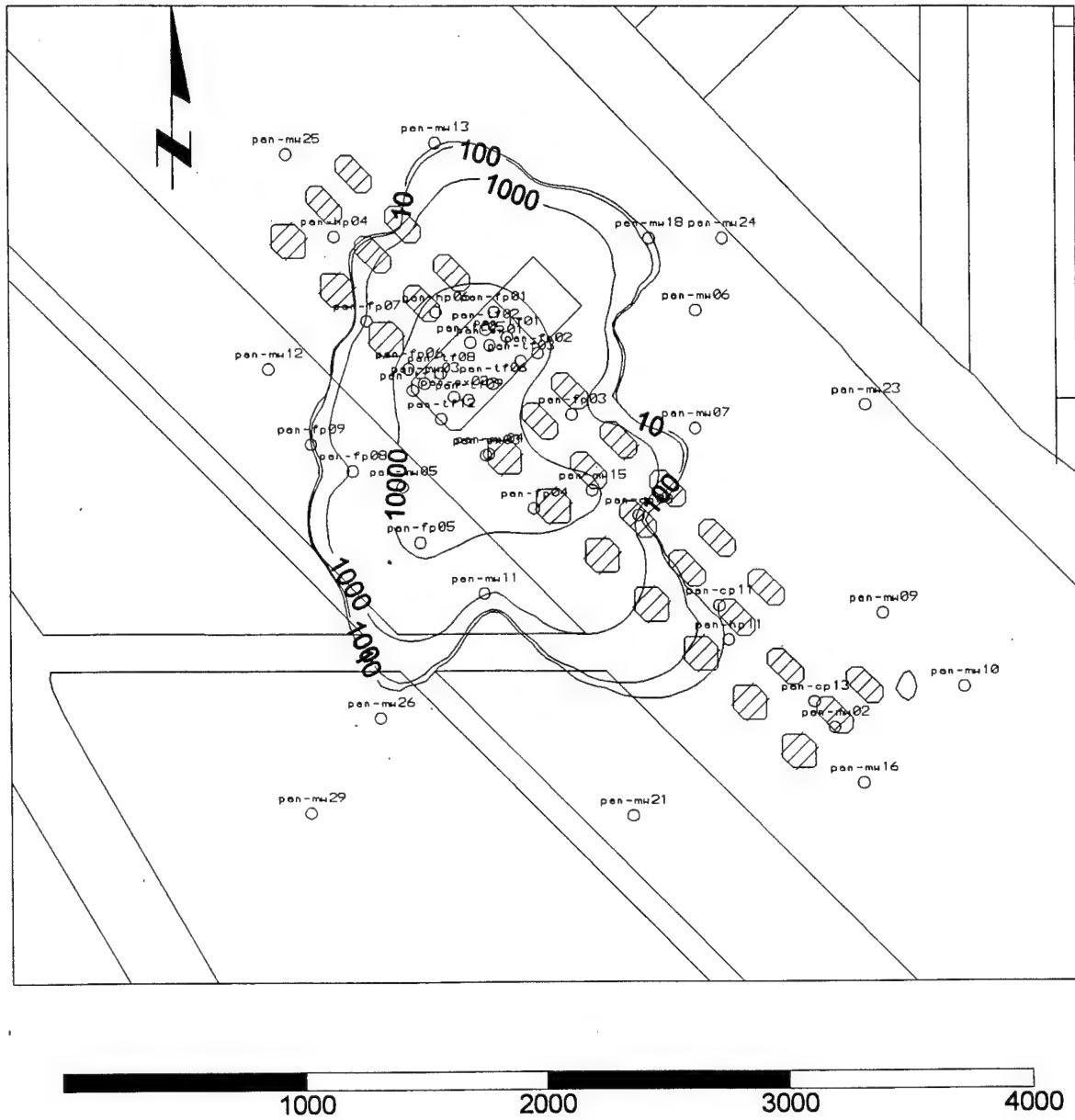
Figure A-38. Toluene concentrations in groundwater at OU 3 for Quarter 4 (approximately 3/93).

Toluene concentrations (ug/L), 5th Quarter
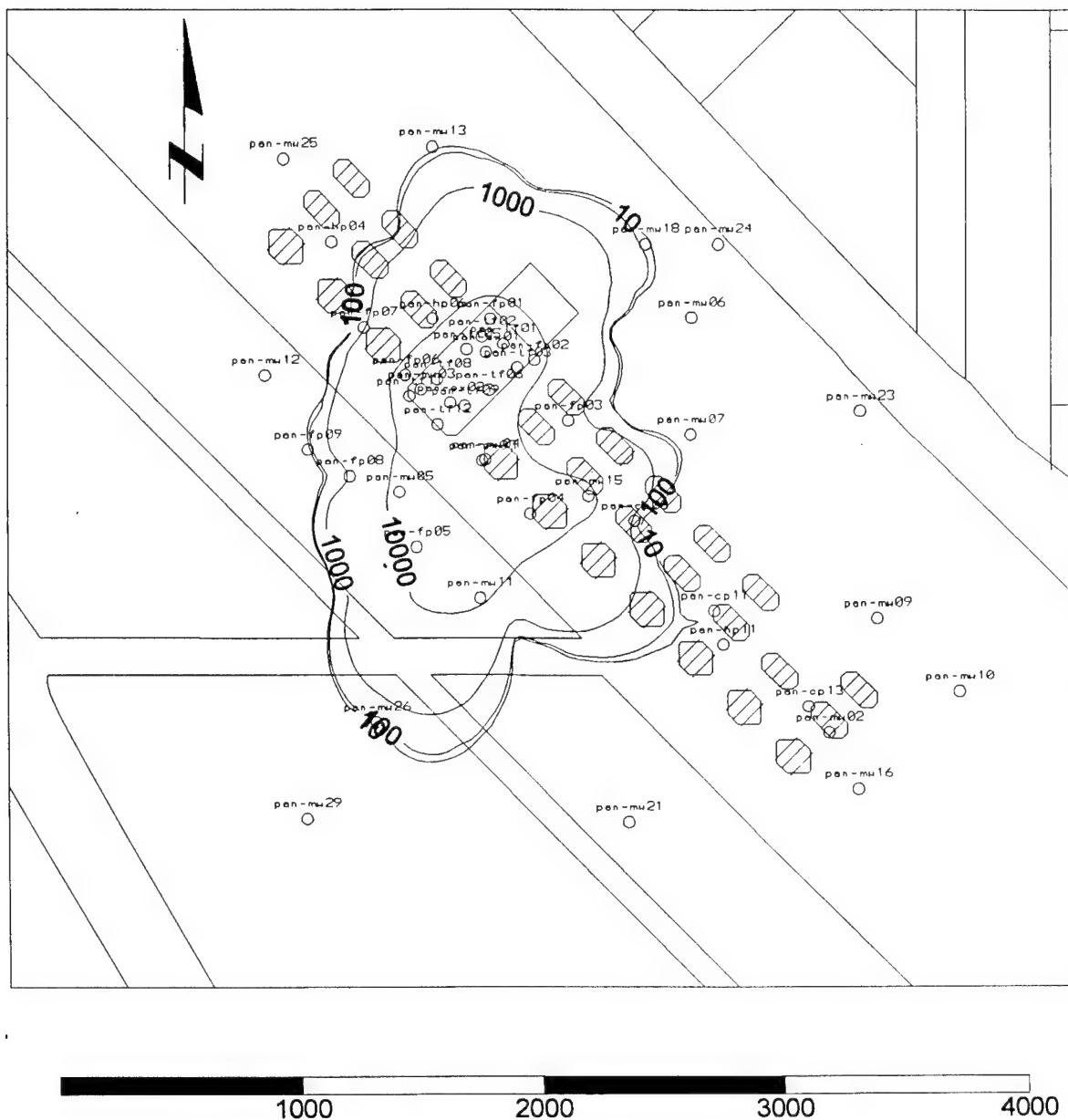
Figure A-39. Toluene concentrations in groundwater at OU 3 for Quarter 5 (approximately 6/93).

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Toluene concentrations (ug/L), 6th Quarter
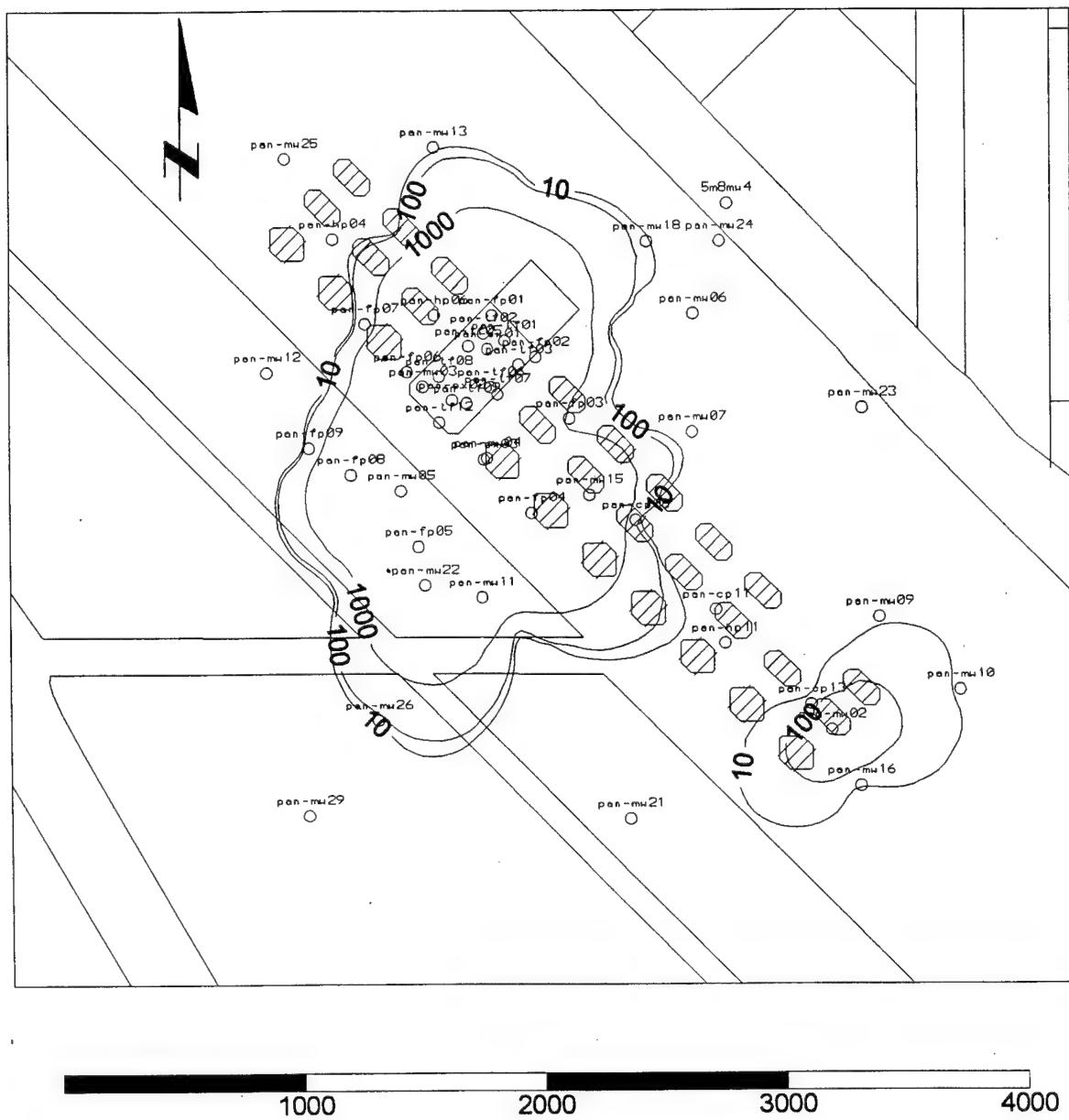
Figure A-40. Toluene concentrations in groundwater at OU 3 for Quarter 6 (approximately 9/93).

Toluene concentrations (ug/L), 7th Quarter
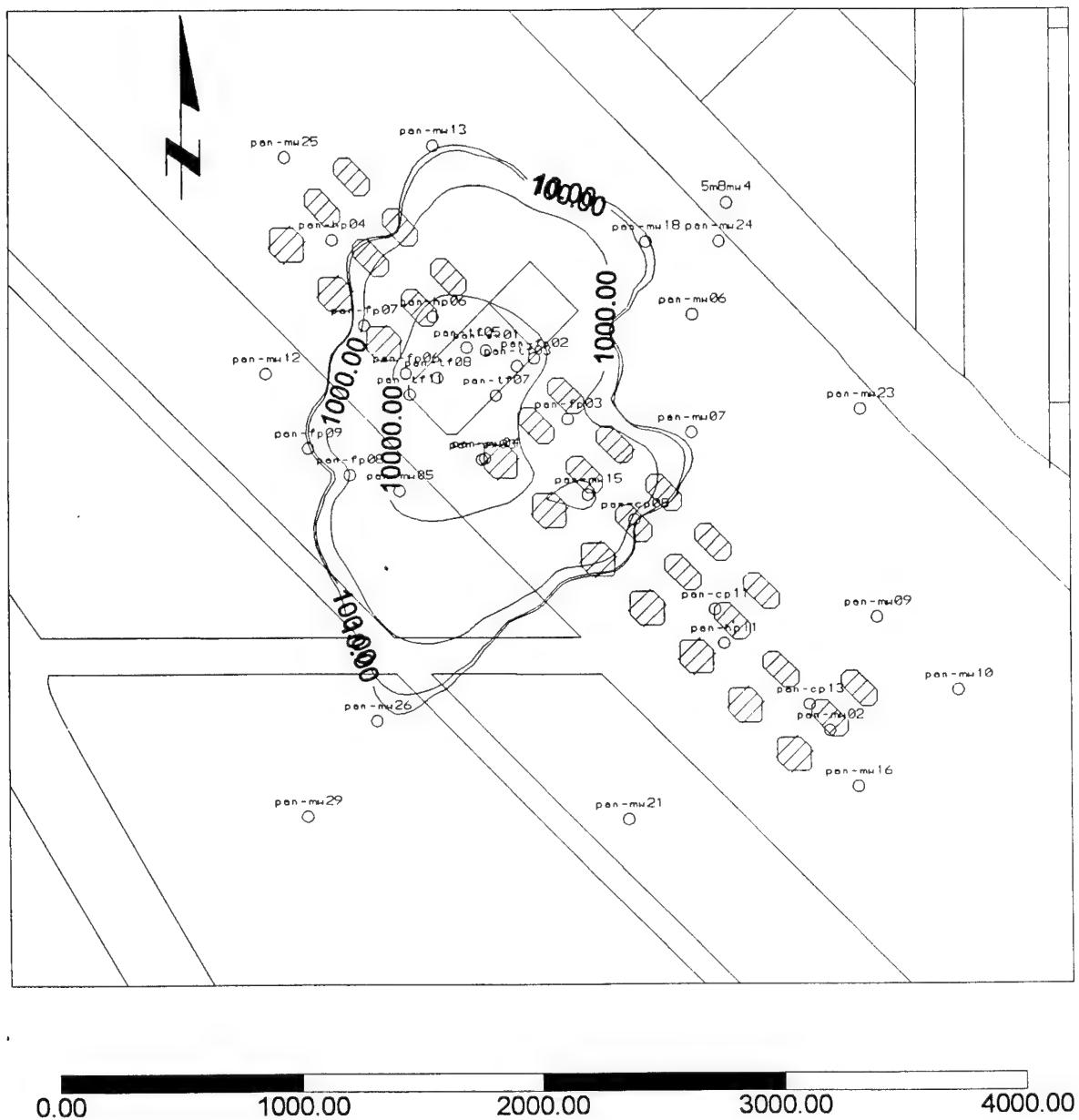
**Figure A-41.** Toluene concentrations in groundwater at OU 3 for Quarter 7 (approximately 12/93).

Toluene concentrations (ug/L), 8th Quarter
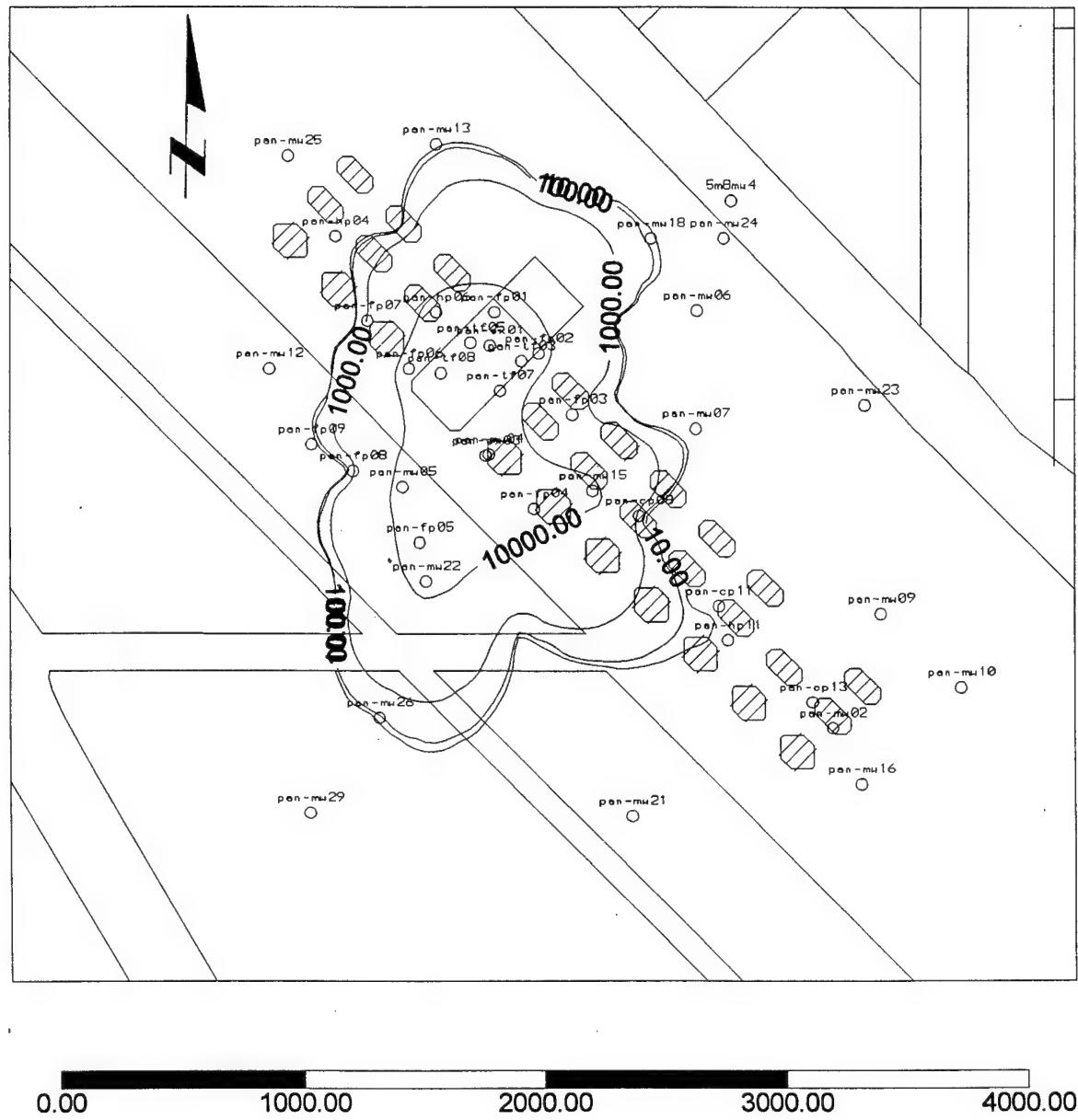
Figure A-42. Toluene concentrations in groundwater at OU 3 for Quarter 8 (approximately 3/94).

Toluene concentrations (ug/L) 9th Quarter
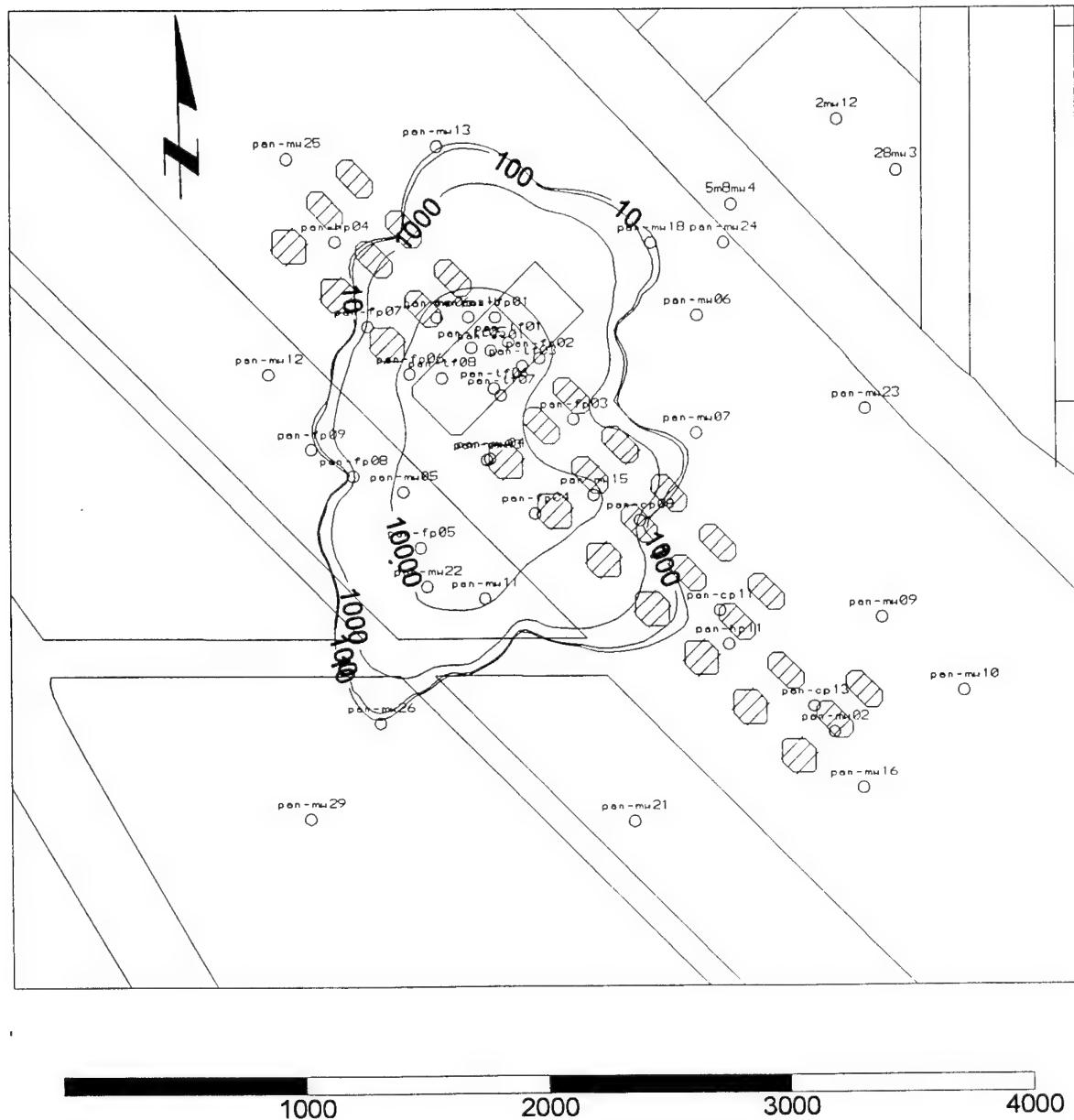
Figure A-43. Toluene concentrations in groundwater at OU 3 for Quarter 9 (approximately 6/94).

Ethylbenzene concentrations (ug/L), 3rd Quarter
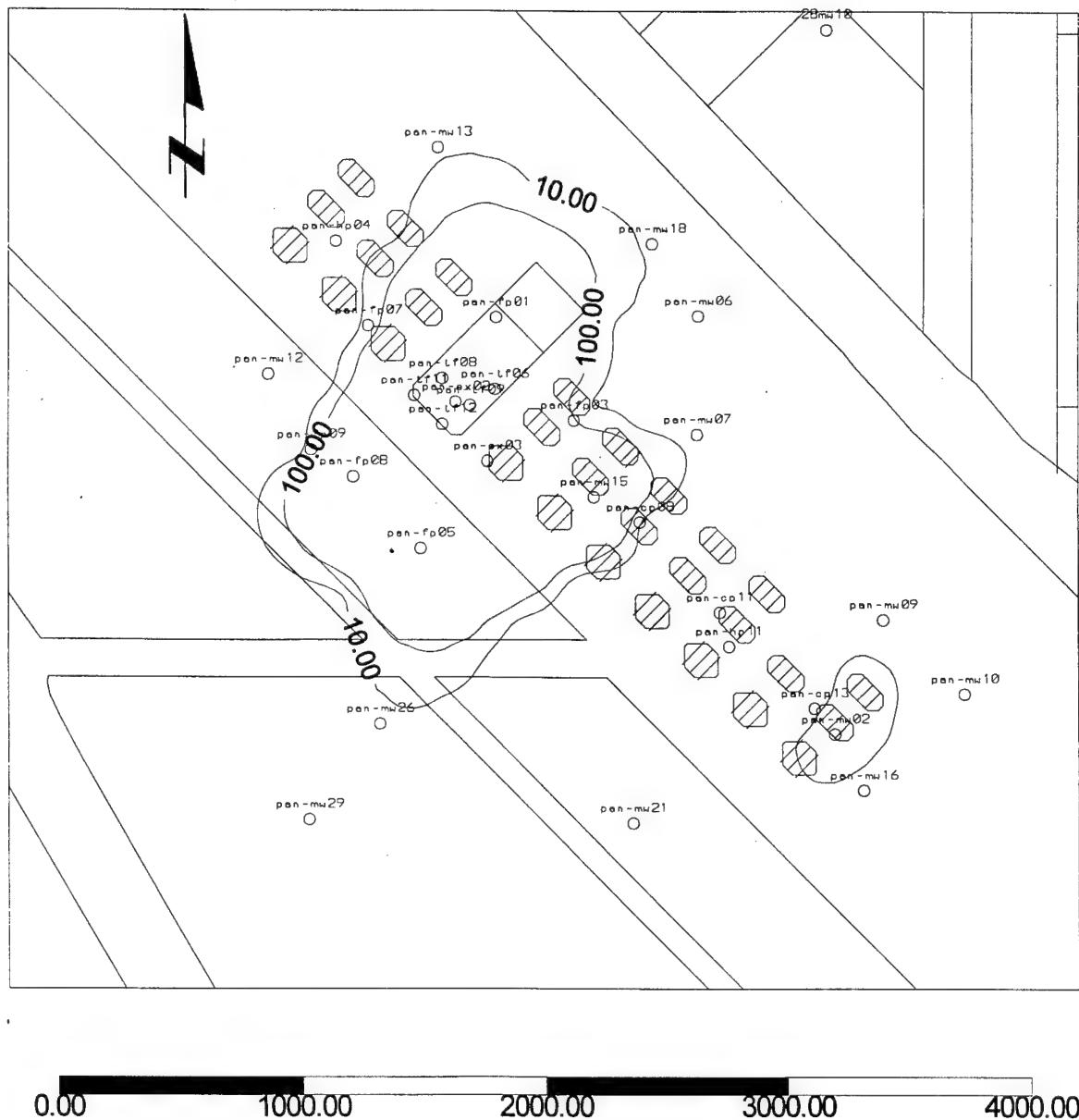
Figure A-44. Ethylbenzene concentrations in groundwater at OU 3 for Quarter 3 (approximately 12/92).

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Ethylbenzene concentrations (ug/L), 4th Quarter
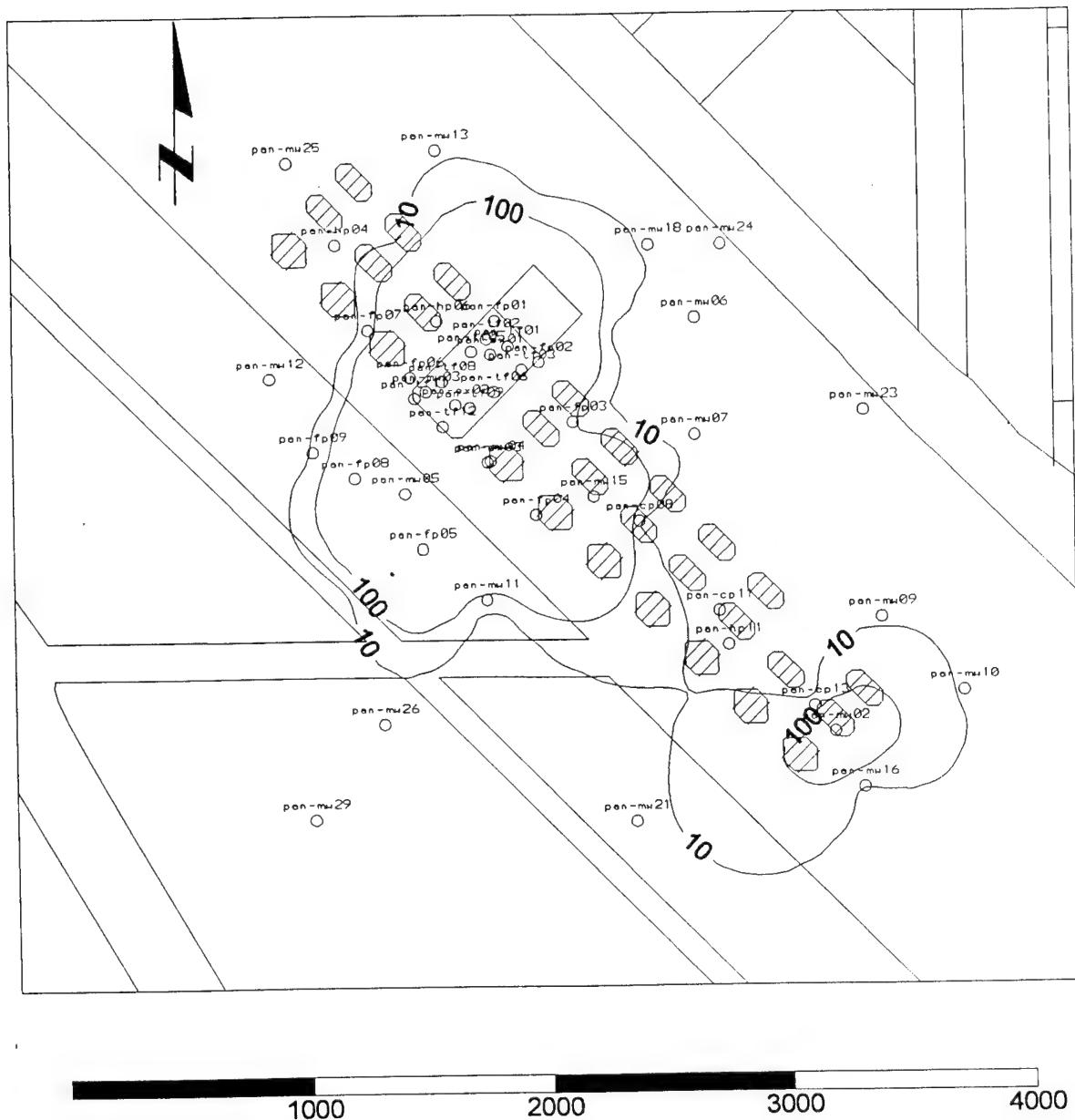
Figure A-45. Ethylbenzene concentrations in groundwater at OU 3 for Quarter 4 (approximately 3/93).

# Ethylbenzene concentrations (ug/L), 5th Quarter
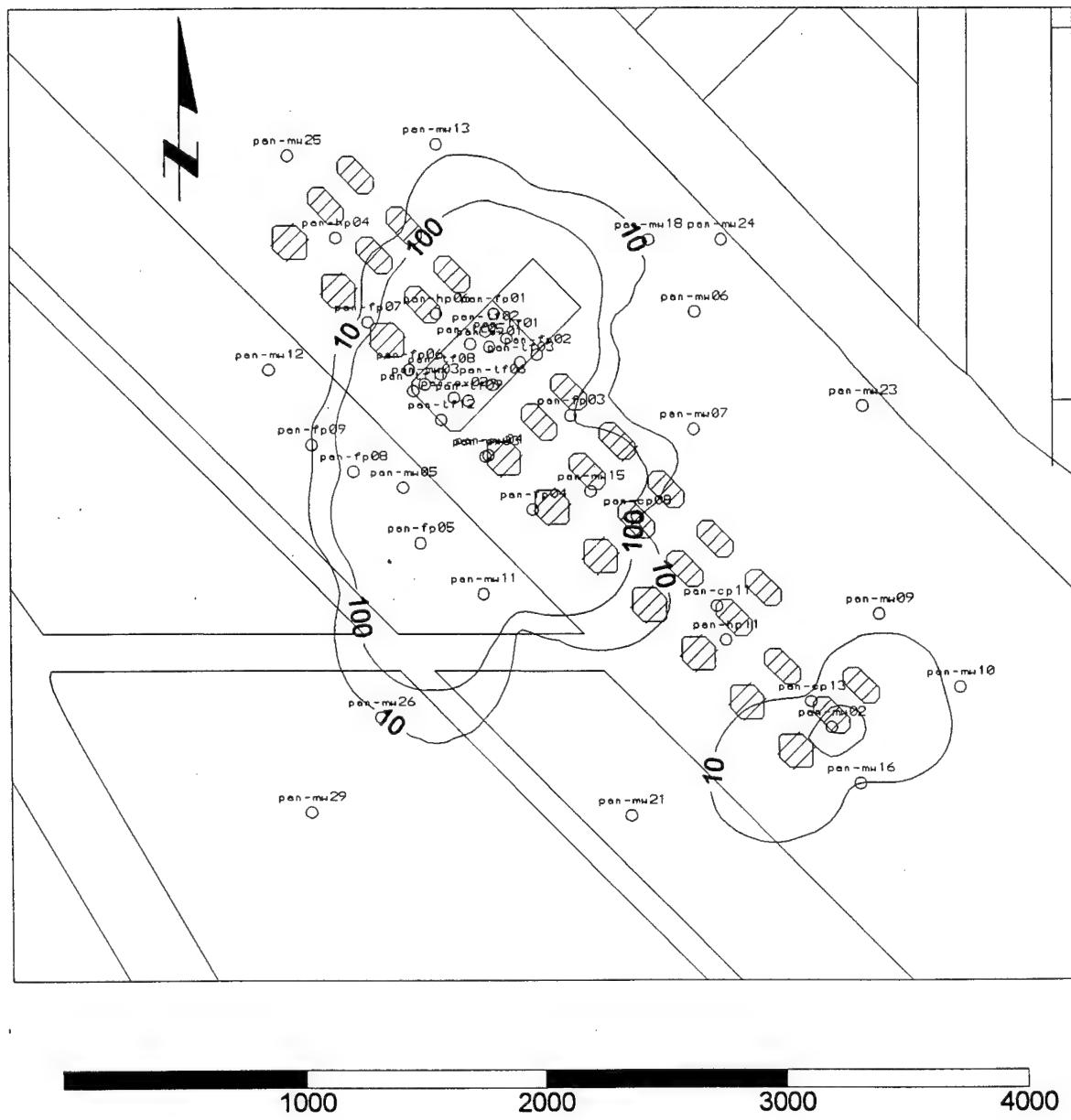
Figure A-46. Ethylbenzene concentrations in groundwater at OU 3 for Quarter 5 (approximately 6/93).

Ethylbenzene concentrations (ug/L), 6th Quarter
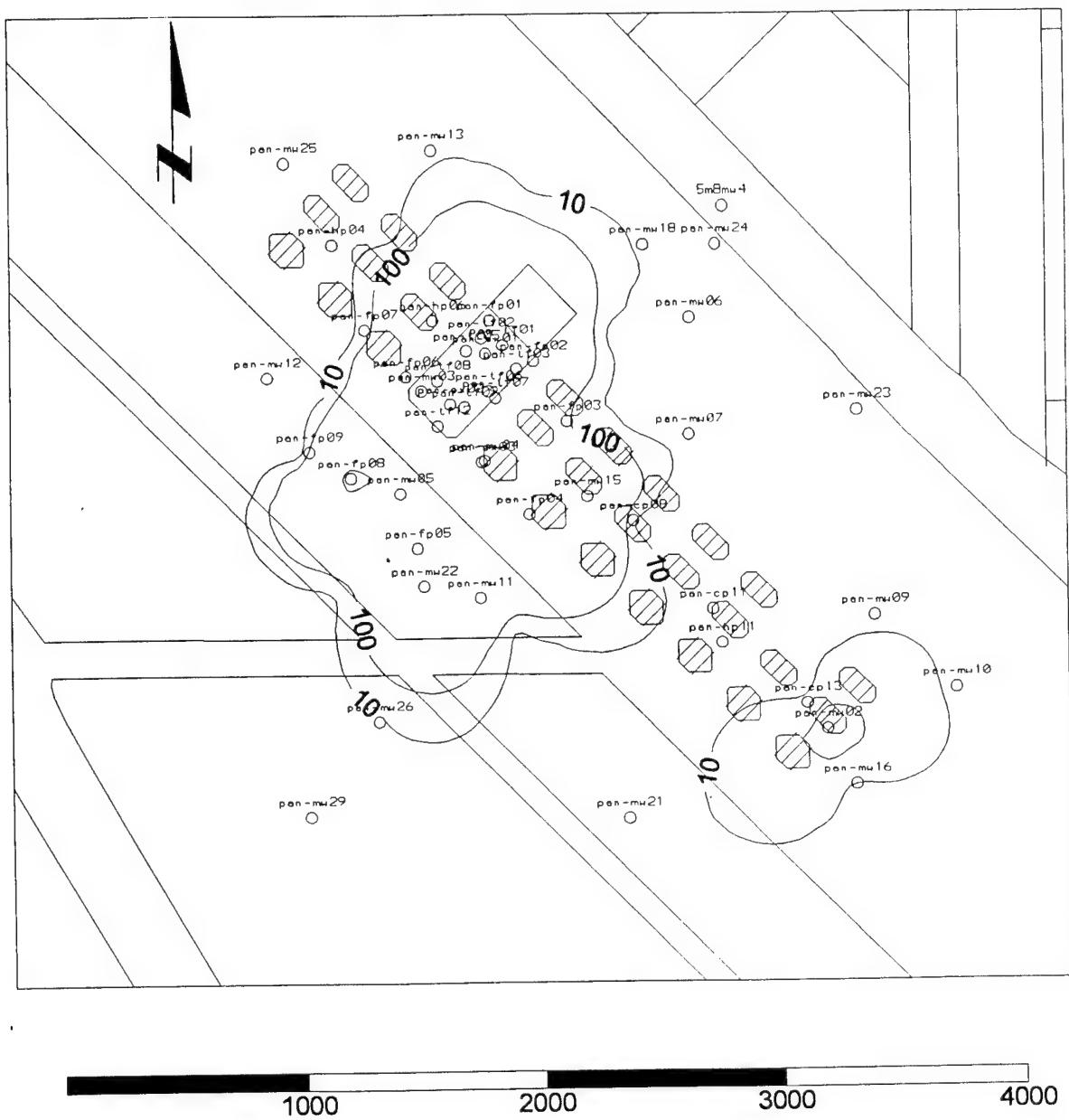
Figure A-47. Ethylbenzene concentrations in groundwater at OU 3 for Quarter 6 (approximately 9/93).

Ethylbenzene concentrations (ug/L), 7th Quarter
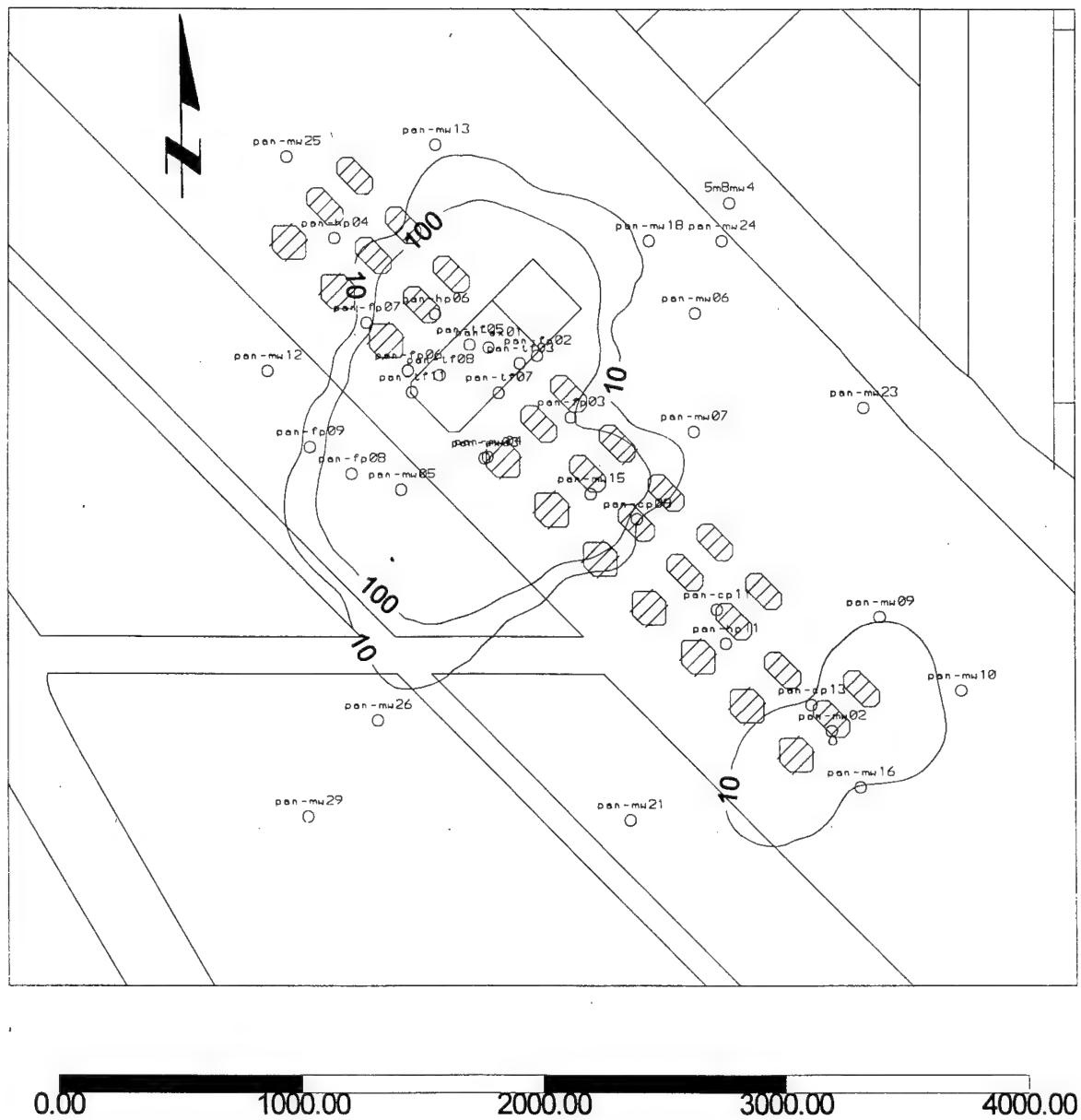
Figure A-48. Ethylbenzene concentrations in groundwater at OU 3 for Quarter 7 (approximately 12/93).

# Ethylbenzene concentrations (ug/L), 8th Quarter
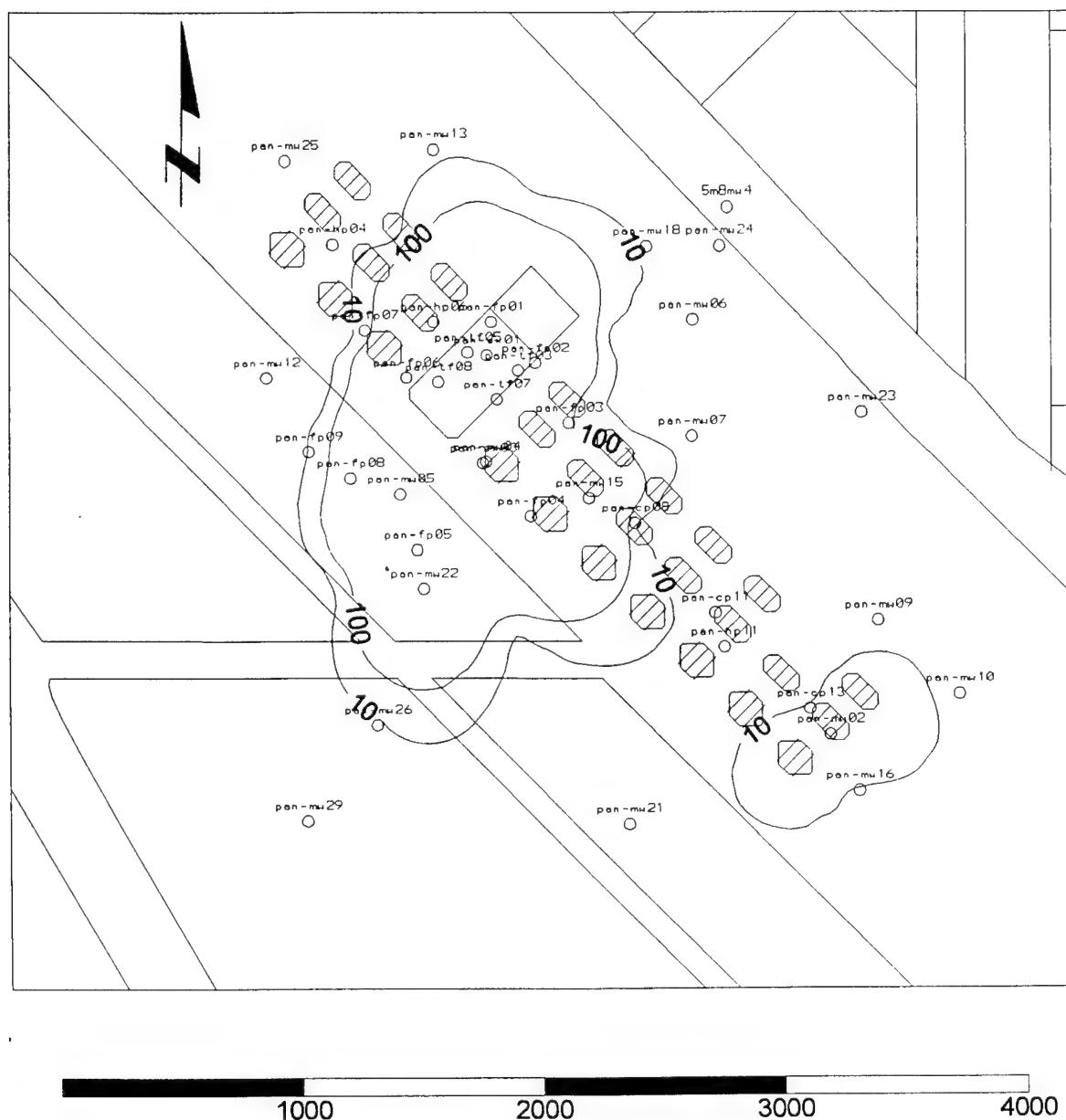
Figure A-49. Ethylbenzene concentrations in groundwater at OU 3 for Quarter 8 (approximately 3/94).

Ethylbenzene concentrations (ug/L) 9th Quarter
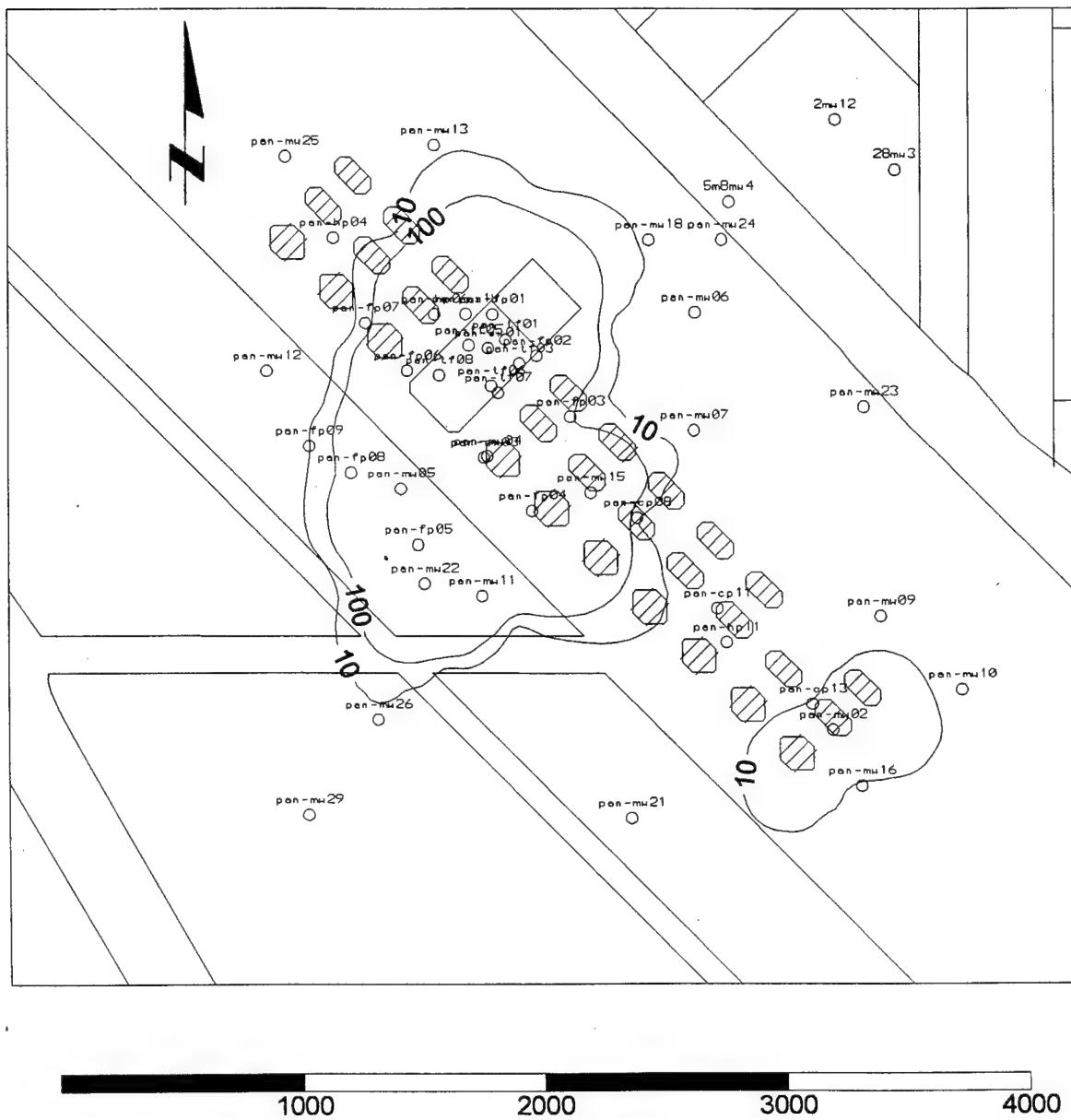
Figure A-50. Ethylbenzene concentrations in groundwater at OU 3 for Quarter 9 (approximately 6/94).

Xylenes (total) concentrations (ug/L), 3rd Quarter
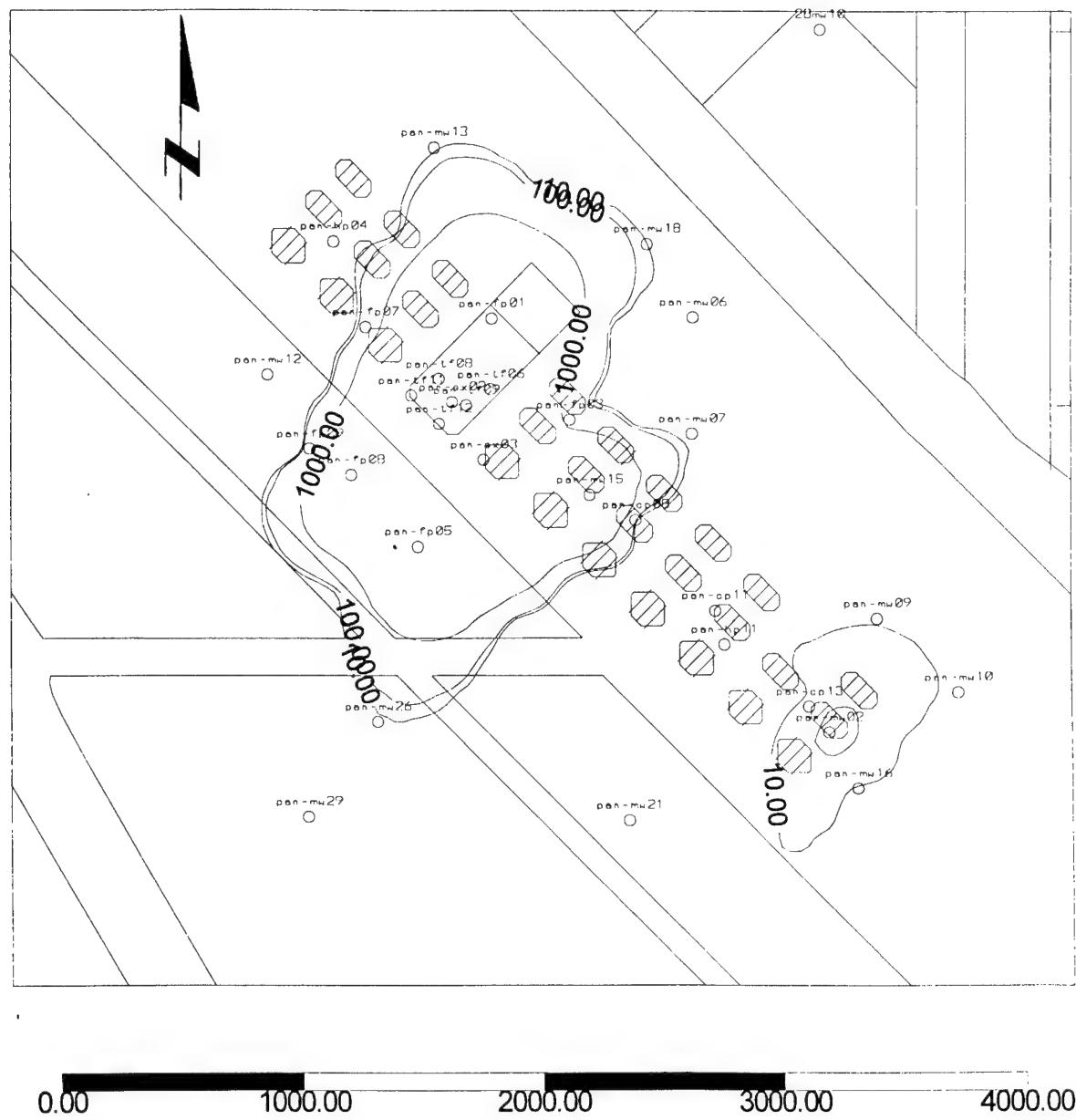
Figure A-51. Total xylenes concentrations in groundwater at OU 3 for Quarter 3 (approximately 12/92).

Total Xylenes concentrations (ug/L), 4th Quarter
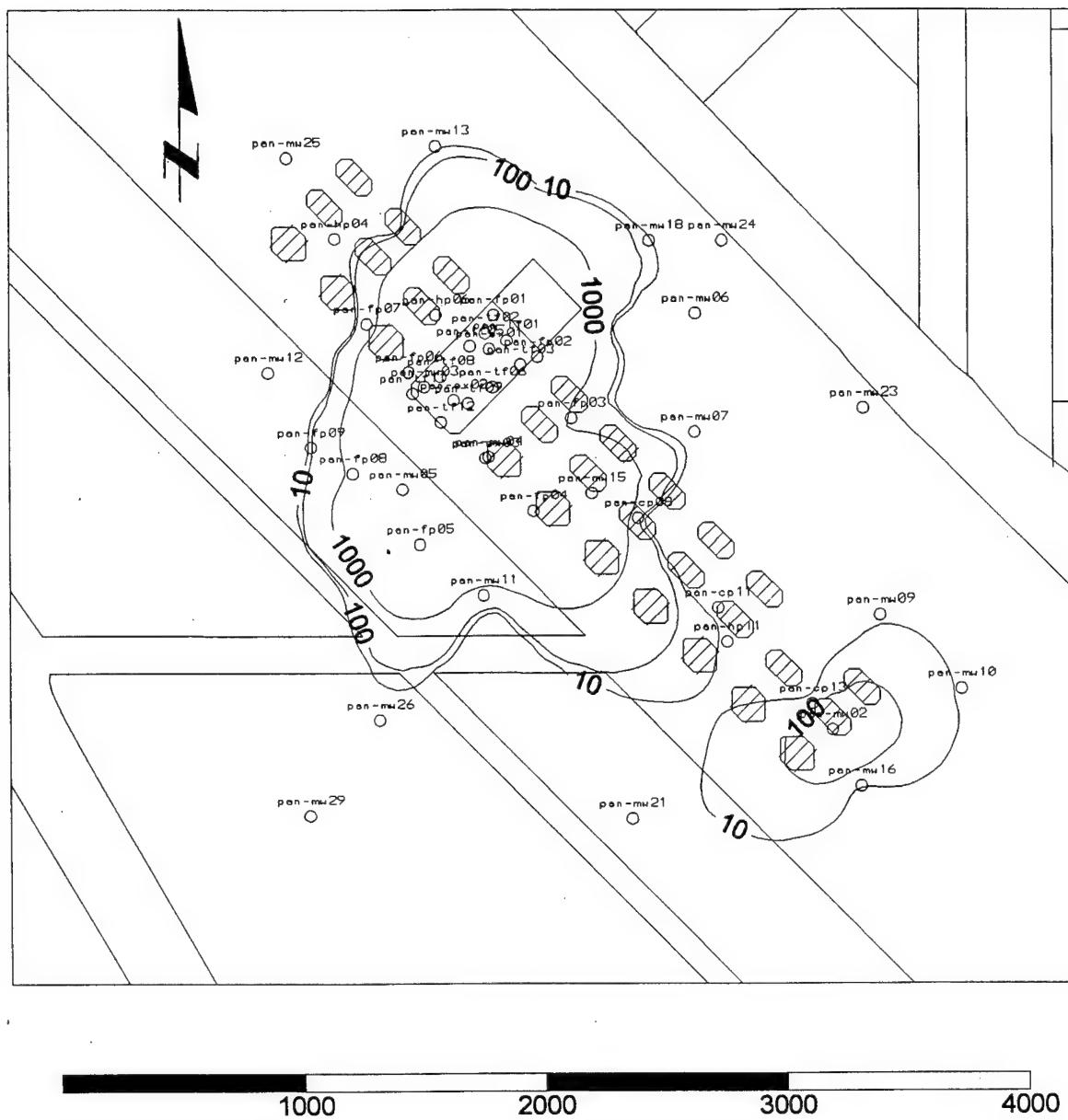
Figure A-52. Total xylenes concentrations in groundwater at OU 3 for Quarter 4 (approximately 3/93).

Xylenes (total) concentrations (ug/L), 5th Quarter
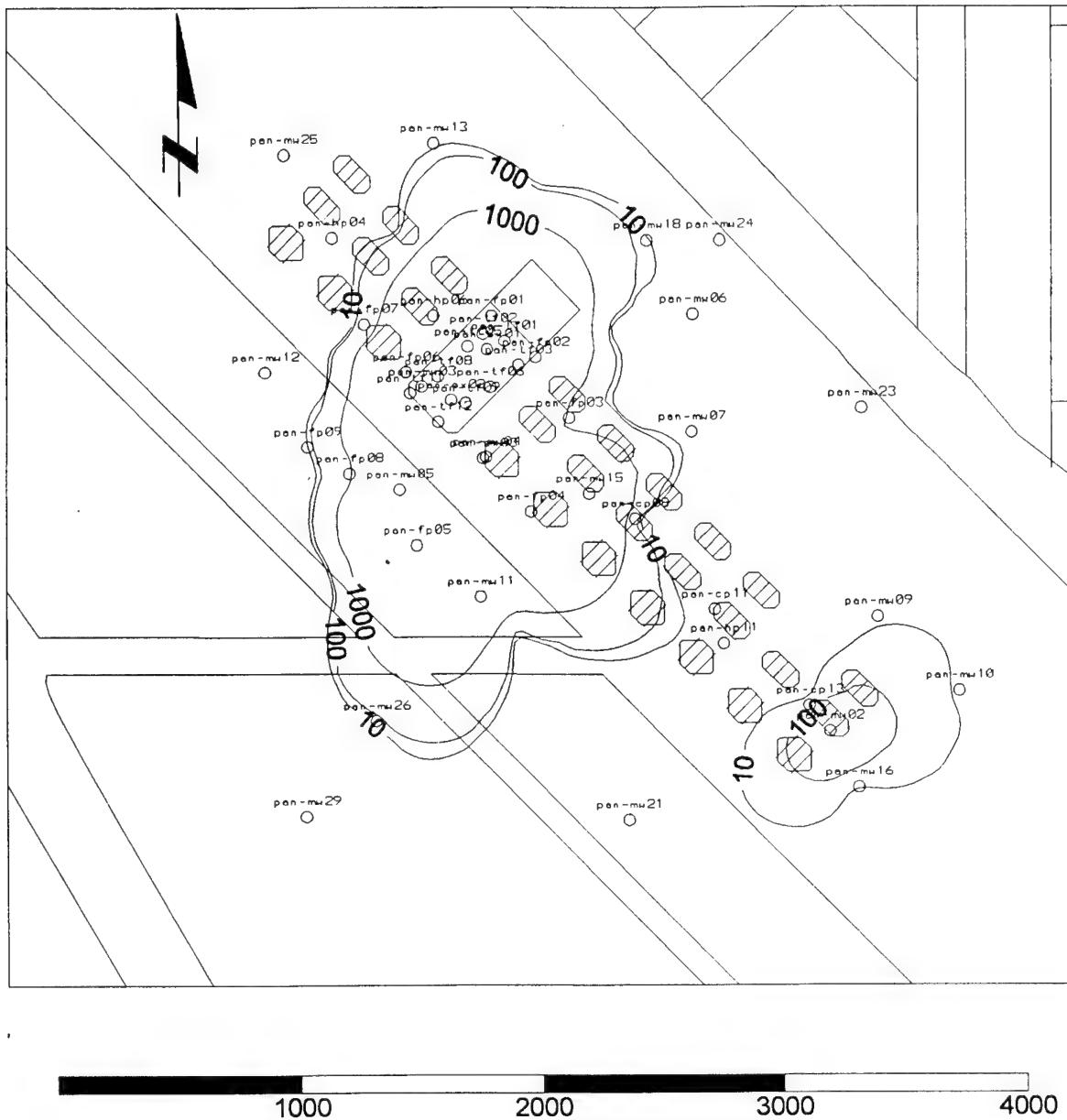
Figure A-53. Total xylenes concentrations in groundwater at OU 3 for Quarter 5 (approximately 6/93).

# Xylene (total) concentrations (ug/L), 6th Quarter
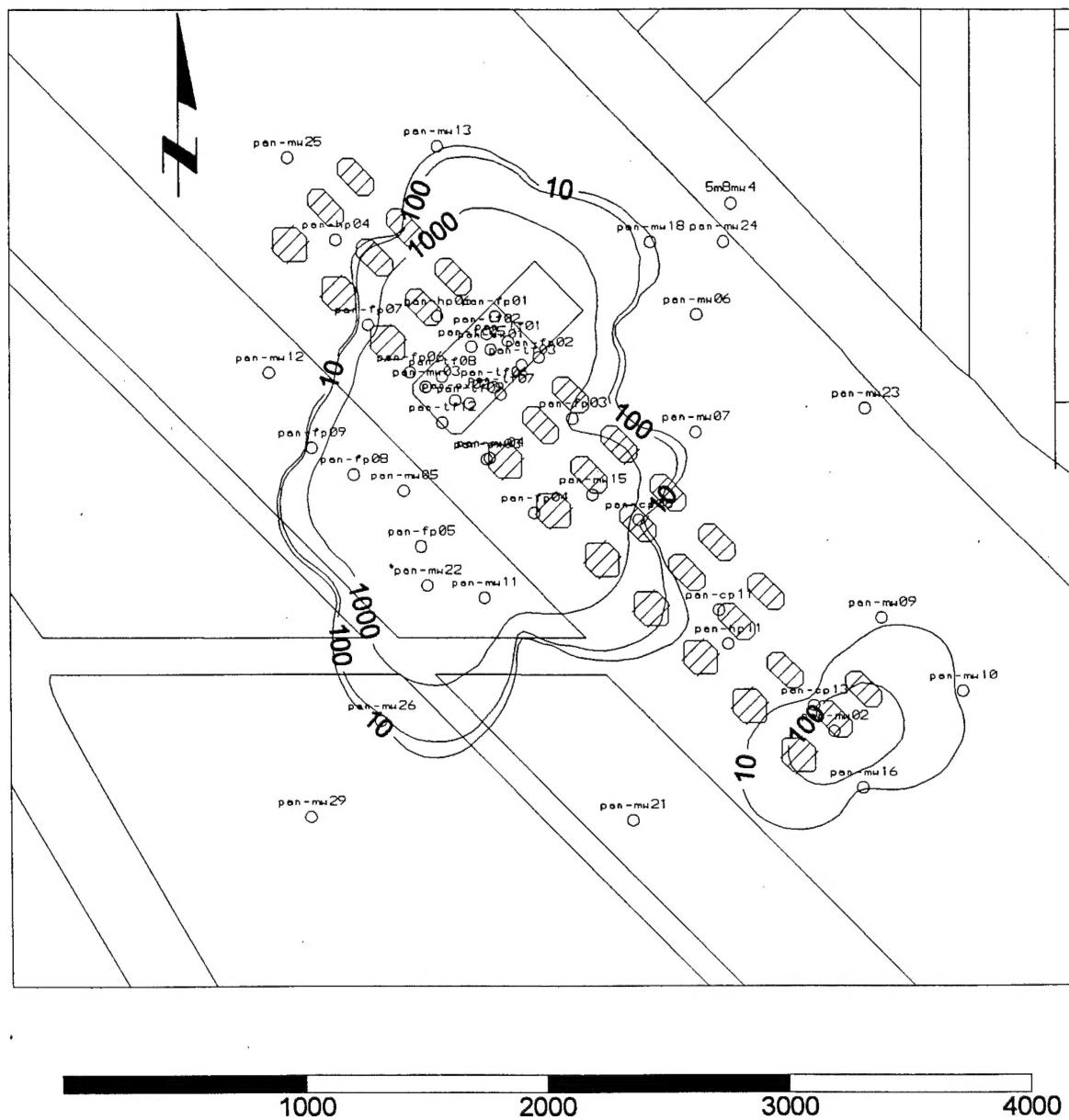
Figure A-54. Total xylenes concentrations in groundwater at OU 3 for Quarter 6 (approximately 9/93).

Xylenes (total) concentrations (ug/L), 7th Quarter
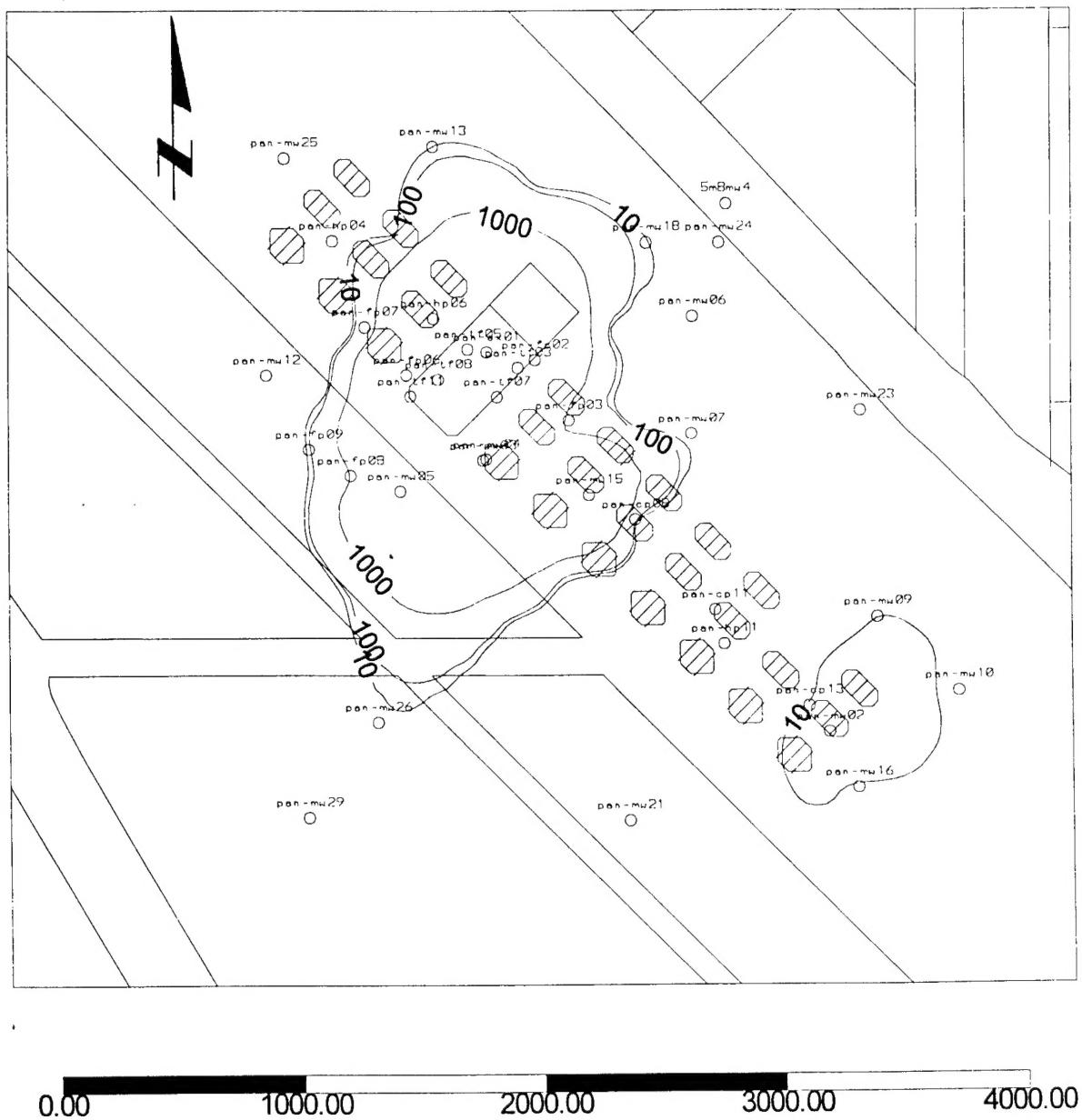
Figure A-55. Total xylenes concentrations in groundwater at OU 3 for Quarter 7 (approximately 12/93).

Xylenes (total) concentrations (ug/L), 8th Quarter
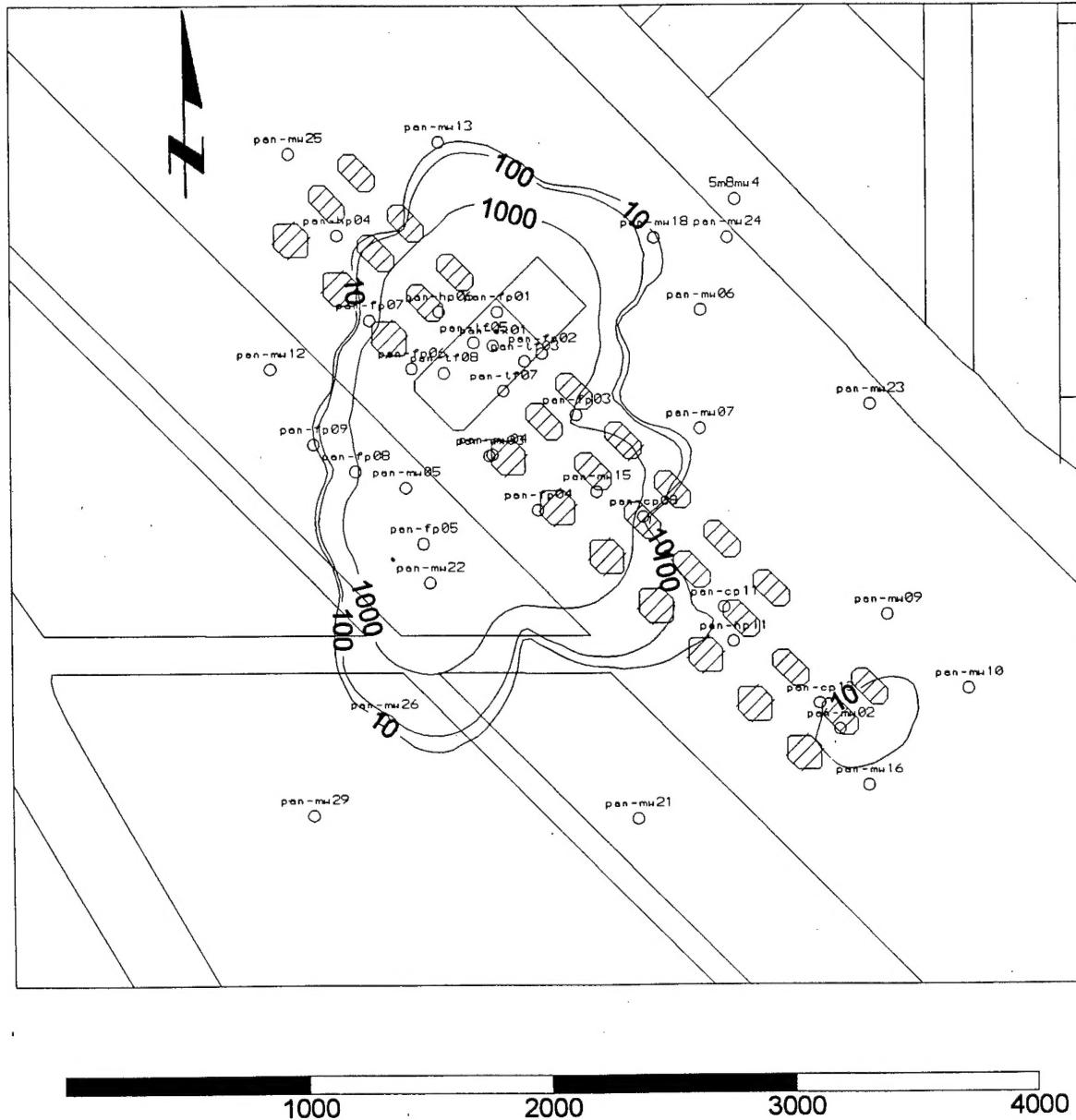

Figure A-56. Total xylenes concentrations in groundwater at OU 3 for Quarter 8 (approximately 3/94).

# Xylenes (total) concentrations (ug/L) 9th Quarter
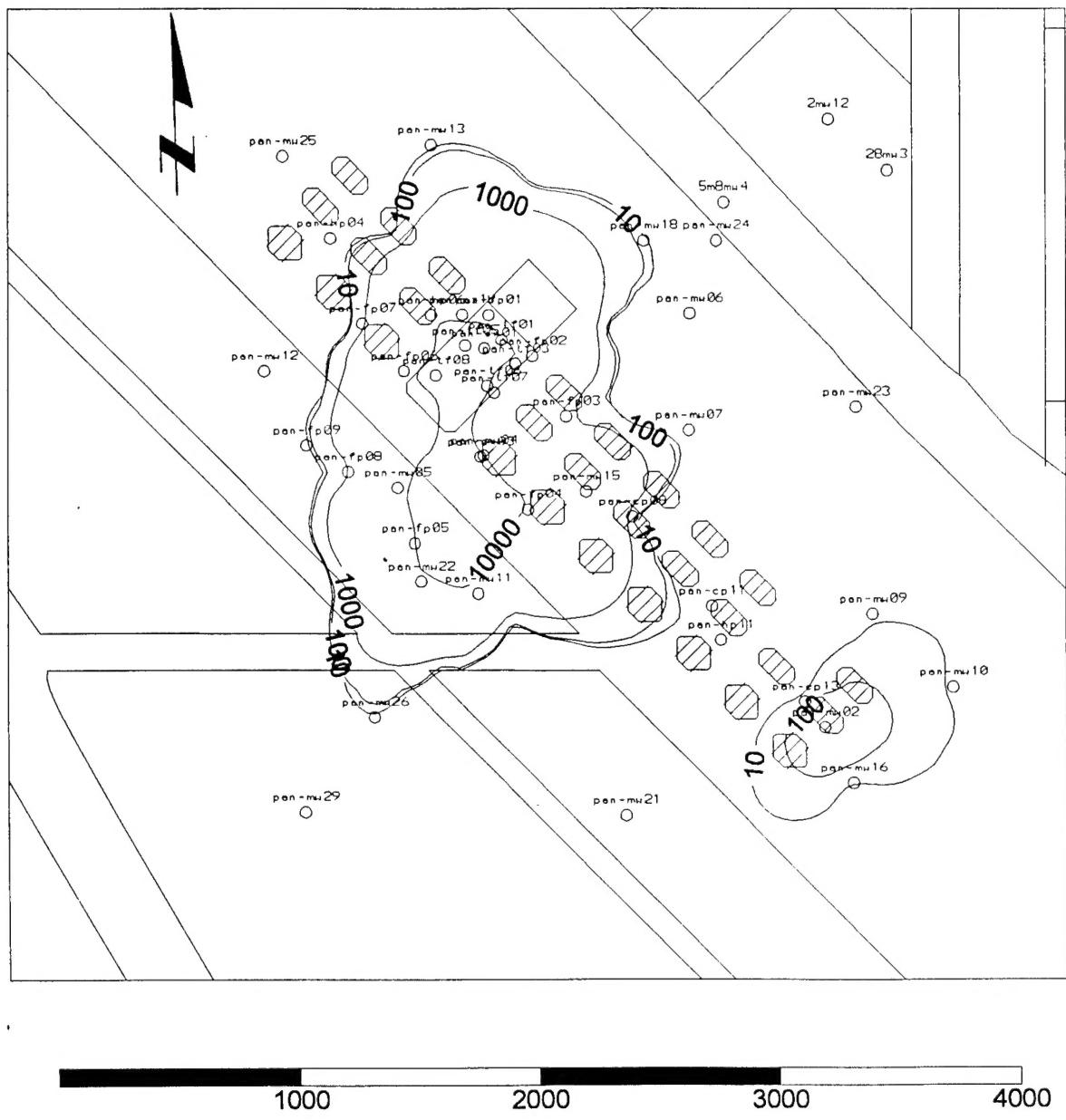
Figure A-57. Total xylenes concentrations in groundwater at OU 3 for Quarter 9 (approximately 6/94).